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Environmental Considerations of Selected Energy Conserving Manufacturing Process Options: Volume XII. Chlor-Alkali Industry Report

Arthur D. Little, Inc, Cambridge, Mass.

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16. ABSTRACT

This study assesses the likelihood of new process technology and new practices being introduced by energy intensive industries and explores the environmental impacts of such changes.

Specifically, Vol. XII examines options in the chlor-alkali industry relating to diaphragm and mercury cell technology, including dimensionally stable anodes, ion-exchange membranes and stabilized asbestos diaphragms in terms of relative process economics and environmental/energy consequences.

Vol. III-XI and Vol. XIII-XV deal with the following industries: iron and steel, petroleum refining, pulp and paper, olefins, ammonia, aluminum, textiles, cement, glass, phosphorus and phosphoric acid, copper, and fertilizers. Vol. I presents the overall summation and identification of research needs and areas of highest overall priority. Vol. II, prepared early in the study, presents and describes the overview of the industries considered and presents the methodology used to select industries.

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Vol. XII. Chlor-alkali Industry Report

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December 1976

ENVIRONMENTAL CONSIDERATIONS OF SELECTED ENERGY CONSERVING MANUFACTURING PROCESS OPTIONS

Volume XII

CHLOR-ALKALI INDUSTRY REPORT

EPA Contract No. 68-03-2198

Project Officer

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This study, consisting of 15 reports, identifies promising industrial processes and practices in 13 energy-intensive industries which, if implemented over the coming 10 to 15 years, could result in more effective utilization of energy resources. The study was carried out to assess the potential environmental/energy impacts of such changes and the adequacy of existing control technology in order to identify potential conflicts with environmental regulations and to alert the Agency to areas where its activities and policies could influence the future choice of alternatives. The results will be used by the EPA's Office of Research and Development to define those areas where existing pollution control technology suffices, where current and anticipated programs adequately address the areas identified by the contractor, and where selected program reorientation seems necessary. Specific data will also be of considerable value to individual researchers as industry background and in decision-making concerning project selection and direction. The Power Technology and Conservation Branch of the Energy Systems-Environmental Control Division should be contacted for additional information on the program.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

EXECUTIVE SUMMARY

The chlor-alkali industry is a large and relatively mature segment of the inorganic chemical industry. In this series of 13 industry studies, the chlor-alkali industry ranked eleventh in terms of both purchased energy usage and potential for viable process changes having significant energy and effluent consequences.

Chlorine and caustic are coproducts of brine electrolysis. There are several dozen important U.S. producers of these chemicals, although the top four producers account for nearly 60% of total production. Current (1974) production levels for these chemicals are on the order of 11 to 12 million tons each. The diffuse end use markets are expected to lead to an average demand growth of approximately 5 to 6 percent per annum over the next decade.

Chlor-alkali plants and production technology have a history of slow evolution in the United States. During the next 15 years, several significant changes are expected. Among the more important are the conversion from existing graphite electrodes to dimensionably stable anodes (DSA), the development of ion-exchange membrane technology and the replacement of deposited asbestos diaphragms with stabilized asbestos diaphragms. No new mercury cell plants are expected to be built because of inherent problems with pollution and high electrical energy requirements.

The effect of these and other changes over the long run will be to reduce average energy consumption for the industry by 15 percent or more per ton of product. None of the process changes are expected, in themselves, to create any new pollution hazards, but rather they are expected to further reduce the level of industry effluents. For example, the already small volume of chlorinated organic waste associated with the use of graphite anodes will be eliminated, as will the solid waste from spent anodes and diaphragms. The introduction of DSA technology will reduce the amount of gas vented from the chlorine liquefaction system.

Basic research needs in the industry center around further reduction in process wastes, further reduction in energy requirements and further decoupling of chlorine and caustic production to allow a closer supply/demand balance for each. It is recommended that research, development, or demonstration efforts be directed at promoting the work already underway in these areas.

This report was submitted in partial fulfillment of contract 68-03-2198 by Arthur D. Little, Inc. under sponsorship of the U.S. Environmental Protection Agency. This report covers a period from June 9, 1975 to February 9, 1976.

TABLE OF CONTENTS

Page

FOREWORD iii
EXECUTIVE SUMMARY iv
List of Figures vi
List of Tables vii
Acknowledgments ix
Conversion Table xii

I. INTRODUCTION 1
  A. BACKGROUND 1
  B. CRITERIA FOR INDUSTRY SELECTION 1
  C. CRITERIA FOR PROCESS SELECTION 2
  D. SELECTION OF CHLOR-ALKALI INDUSTRY PROCESS OPTIONS 4

II. FINDINGS, CONCLUSIONS AND RECOMMENDATIONS 6

III. INDUSTRY OVERVIEW 9
  A. DESCRIPTION 9
    1. Industry Sectors 11
    2. Plant Characteristics 13
    3. Type of Integration 15
  B. ECONOMIC OUTLOOK 15
    1. Historical Trends and Projected Growth 15
    2. Technical and Economic Life of Manufacturing Facilities 19

IV. COMPARISON OF CURRENT AND ALTERNATIVE PROCESSES 20
  A. BASIS FOR SELECTING PROCESSES 20
  B. COMPARISON OF PRESENT PROCESS WITH ALTERNATIVES 21
    1. Base Line Process - Graphite Anode Diaphragm Cell 21
    2. Current Effluent Situation 28
    3. Modified Anodes 44
    4. Modified Diaphragms 48
    5. Comparison of Mercury and Diaphragm Cells 52

V. IMPLICATIONS OF POTENTIAL INDUSTRY CHANGES 61
  A. PROBABLE CHANGES 61
  B. ENVIRONMENTAL IMPLICATIONS 61

APPENDIX A - INDUSTRY STRUCTURE 66

APPENDIX B - CHLOR-ALKALI GLOSSARY 77

LIST OF FIGURES

Number		Page
IV-1	Diaphragm Cell Process	22
IV-2	Mercury Cell Process	53
A-1	Operating Chlorine and Alkali Plants in the Unites States and Canada - January 1, 1975	67

LIST OF TABLES

Number		Page
I-1	Summary of 1971 Energy Purchased in Selected Industry Sectors	3
II-1	Comparison of Base Line and Alternative Processes	7
III-1	U.S. Chlorine Producers and Capacities (short tons per day - 1974)	9
III-2	U.S. Caustic Soda Producers and Capacities (short tons per day - 1974)	10
III-3	1974 U.S. Chlorine Demand Pattern	11
III-4	1974 U.S. Caustic Soda Demand Pattern	12
III-5	Chlor-Alkali Industry: Trends and Projections 1967-75 (In millions of dollars except as noted)	14
III-6	U.S. Chlorine Production, Trade, and Apparent Consumption, 1955-74 (Millions of Short Tons)	16
III-7	U.S. Caustic Soda Production, Trade, and Apparent Consumption, 1955-74 (Millions of Short Tons)	17
III-8	U.S. Soda Ash Production, Trade, and Apparent Consumption, 1955-74 (Millions of Short Tons, 100% Na_2CO_3)	18
IV-1	Waste Streams From Diaphragm Cell Process	23
IV-2	Estimated Production Cost of Chlorine and Caustic Soda	26
IV-3	Raw Waste Loads From Mercury Cell Process Based on a Survey of 21 Facilities (lb/1000 lb chlorine)	30
IV-4	Wastewater Treatment Cost Estimates - Diaphragm Cell Chlor-Alkali (1000 ton/day capacity - 360 days/year)	35
IV-5	Wastewater Treatment Cost Estimates - Mercury Cell Chlor-Alkali (1000 ton/day capacity - 360 days/year)	36

LIST OF TABLES (Cont.)

Number		Page
IV-6	Chlorine Emissions Form Liquefaction Blow Gases in Diaphragm- and Mercury-Cell Plants	40
IV-7	Estimated Production Cost of Chlorine and Caustic Soda	45
IV-8	Power Savings Effected by Stabilized Diaphragm in H-4 DSA Cells	49
IV-9	Estimated Energy Savings With Advanced Ion Exchange Membrane Cell	51
IV-10	Waste Streams From Modern Mercury Cell Process	54
IV-11	Estimated Production Cost of Chlorine and Caustic Soda	57
IV-12	Energy Comparison of Mercury and Diaphragm Cells	59
V-1	Environmental Implications of Changes in Diaphragm Cells	62
A-1	SIC 2812 Alkalies and Chlorine, Distribution of Establishments	68
A-2	SIC 2812 Alkalies and Chlorine, Distribution of Plant Sizes	69
A-3	SIC 2812 Alkalies and Chlorine, Distribution of Plant Ages	70
A-4	SIC 2812 Alkalies and Chlorine, Distribution of Processes	71
A-5	SIC 2812 Alkalies and Chlorine, Distribution of Production	72
A-6	Chlorine Production Routes - U.S. and Canada	73
A-7	Chlorine Capacity and Production in the United States	74
A-8	U.S. Soda Ash Producers and Capacities (short tons per year - 1973)	75
A-9	U.S. Caustic Potash Producers and Capacities (short tons per year - 1973)	76
A-10	U.S. Sodium Bicarbonate Producers and Capacities (short tons per year - 1973)	76

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During the course of the study we also had occasion to contact many individuals within industry and trade associations. Where appropriate we have made reference to these contacts within the various reports. Frequently, however, because of the study's emphasis on future developments with comparative assessments of new technology, information given to us was of a confidential nature or was supplied to us with the understanding that it was not to be credited. Therefore, we extend a general thanks to all those whose comments were valuable to us for their interest in and contribution to this study.

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ENGLISH-METRIC (SI) CONVERSION FACTORS

To Convert From	To	Multiply By
Acre	Metre^2	4,046
Atmosphere (normal)	Pascal	101,325
Barrel (42 gal)	Metre^3	0.1589
British Thermal Unit	Joule	1,055
Centipoise	Pascal-second	0.001
Degree Fahrenheit	Degree Celsius	$t^\circ_c = (t^\circ_F - 32)/1.8$
Degree Rankine	Degree Kelvin	$t^\circ_K = t^\circ_R/1.8$
Foot	Metre	0.3048
Foot^3/minute	Metre^3/sec	0.0004719
Foot^3	Metre^3	0.02831
Foot^2	Metre^2	0.09290
Foot/sec	Metre/sec	0.3048
Foot^2/hr	Metre^2/sec	0.00002580
Gallon (U.S. liquid)	Metre^3	0.003785
Horsepower (550 ft-lbf/sec)	Watt	745.7
Horsepower (electric)	Watt	746.0
Horsepower (metric)	Watt	735.5
Inch	Metre	0.02540
Kilowatt-hour	Joule	3.60×10^6
Litre	Metre^3	1.000×10^{-3}
Micron	Metre	1.000×10^{-6}
Mil	Metre	0.00002540
Mile (U.S. statute)	Metre	1,609
Poise	Pascal-second	0.1000
Pound force (avdp)	Newton	4.448
Pound mass (avdp)	Kilogram	0.4536
Ton (assay)	Kilogram	0.02916
Ton (long)	Kilogram	1,016
Ton (metric)	Kilogram	1,000
Ton (short)	Kilogram	907.1
Tonne	Kilogram	1,000

Source: American National Standards Institute, "Standard Metric Practice Guide," March 15, 1973. (ANS72101-1973) (ASTM Designation E380-72)

I. INTRODUCTION

A. BACKGROUND

Industry in the United States purchases about 27 quads* annually, approximately 40% of total national energy usage.** This energy is used for chemical processing, raising steam, drying, space cooling and heating, process stream heating, and miscellaneous other purposes.

In many industrial sectors energy consumption can be reduced significantly by better "housekeeping" (i.e., shutting off standby furnaces, better thermostat control, elimination of steam and heat leaks, etc.) and greater emphasis on optimization of energy usage. In addition, however, industry can be expected to introduce new industrial practices or processes either to conserve energy or to take advantage of a more readily available or less costly fuel. Such changes in industrial practices may result in changes in air, water or solid waste discharges. The EPA is interested in identifying the pollution loads of such new energy-conserving industrial practices or processes and in determining where additional research, development, or demonstration is needed to characterize and control the effluent streams.

B. CRITERIA FOR INDUSTRY SELECTION

In the first phase of this study we identified industry sectors that have a potential for change, emphasizing those changes which have an environmental/energy impact.

Industries were eliminated from further consideration within this assignment if the only changes that could be envisioned were:

- energy conservation as a result of better policing or "housekeeping,"
- better waste heat utilization,
- fuel switching in steam raising, or
- power generation.

After discussions with the EPA Project Officer and his advisors, industry sectors were selected for further consideration and ranked using:

---

*1 quad = 10^{15} Btu

**purchased electricity valued at an approximate fossil fuel equivalent of 10,500 Btu/kWh

- Quantitative criteria based on the gross amount of energy (fossil fuel and electric) purchased by industry sector as found in U.S. Census figures and from information provided from industry sources. The chlor-alkali industry purchased 0.24 quads out of the 12.14 quads purchased in 1971 by the 13 industries selected for study, or 9% of the 27 quads purchased by all industry (see Table I-1).

- Qualitative criteria relating to probability and potential for process change, and the energy and effluent consequences of such changes.

In order to allow for as broad a coverage of technologies as possible, we then reviewed the ranking, eliminating some industries in which the process changes to be studied were similar to those in another industry planned for study. We believe the final ranking resulting from these considerations identifies those industry sectors which show the greatest possibility of energy conservation via process change. Further details on this selection process can be found in the Industry Priority Report prepared under this contract (Volume II).

On the basis of this ranking method, the chlor-alkali industry appeared in eleventh place among the 13 industrial sectors listed.

C. CRITERIA FOR PROCESS SELECTION

In this study we have focused on identifying changes in the primary production processes which have clearly defined pollution consequences. In selecting those to be included in this study, we have considered the needs and limitations of the EPA as discussed more completely in the Industry Priority Report mentioned above. Specifically, energy conservation has been defined broadly to include, in addition to process changes, conservation of energy or energy form (gas, oil, coal) by a process or feedstock change. Natural gas has been considered as having the highest energy form value followed in descending order by oil, electric power, and coal. Thus, a switch from gas to electric power would be considered energy conservation because electric power could be generated from coal, existing in abundant reserves in the United States in comparison to natural gas. Moreover, pollution control methods resulting in energy conservation have been included within the scope of this study. Finally, emphasis has been placed on process changes with near-term rather than long-term potential within the 15-year span of time of this study.

In addition to excluding from consideration better waste heat utilization, "housekeeping," power generation, and fuel switching, as mentioned above, certain options have been excluded to avoid duplicating work being funded under other contracts and to focus this study more strictly on "process changes." Consequently, the following have also not been considered to be within the scope of work:

- Carbon monoxide boilers (however, unique process vent streams yielding recoverable energy could be mentioned);

- Fuel substitution in fired process heaters;

- Mining and milling, agriculture, and animal husbandry;

TABLE I-1

SUMMARY OF 1971 ENERGY PURCHASED IN SELECTED INDUSTRY SECTORS

	Industry Sector	10^{15} Btu/Yr	SIC Code In Which Industry Found
1.	Blast furnaces and steel mills	3.49(1)	3312
2.	Petroleum refining	2.96(2)	2911
3.	Paper and allied products	1.59	26
4.	Olefins	0.984(3)	2818
5.	Ammonia	0.63(4)	287
6.	Aluminum	0.59	3334
7.	Textiles	0.54	22
8.	Cement	0.52	3241
9.	Glass	0.31	3211, 3221, 3229
10.	Alkalies and chlorine	0.24	2812
11.	Phosphorus and phosphoric acid production	0.12(5)	2819
12.	Primary copper	0.081	3331
13.	Fertilizers (excluding ammonia)	0.078	287

(1) Estimate for 1967 reported by FEA Project Independence Blueprint, p. 6-2, USGPO, November 1974.

(2) Includes captive consumption of energy from process byproducts (FEA Project Independence Blueprint)

(3) Olefins only, includes energy of feedstocks: ADL estimates

(4) Ammonia feedstock energy included: ADL estimates

(5) ADL estimates

Source: 1972 Census of Manufactures, FEA Project Independence Blueprint, USGPO, November 1974, and ADL estimates.

- Substitution of scrap (such as iron, aluminum, glass, reclaimed textiles and paper) for virgin materials;
- Production of synthetic fuels from coal (low- and high-Btu gas, synthetic crude, synthetic fuel oil, etc.); and
- All aspects of industry-related transportation (such as transportation of raw material).

D. SELECTION OF CHLOR-ALKALI INDUSTRY PROCESS OPTIONS

Within each industry, the magnitude of energy use was an important criterion in judging where the most significant energy savings might be realized, since reduction in energy use reduces the amount of pollution generated in the energy production step. Guided by this consideration, candidate options for in-depth analysis were identified from the major energy consuming process steps with known or potential environmental problems.

After developing a list of candidate process options, we assessed subjectively

- pollution or environmental consequences of the process change,
- probability or potential for the change, and
- energy conservation consequences of the change.

Even though all of the candidate process options were large energy users, there was wide variation in energy use and estimated pollution loads between options at the top and bottom of the list. A modest process change in a major energy consuming process step could have more dramatic consequences than a more technically significant process change in a process step whose energy consumption is rather modest. Process options were selected for in-depth analysis only if a high probability for process change and pollution consequences in the lesser energy-using process steps was perceived.

Because of the time and scope limitations for this study, we have not attempted to prepare a comprehensive list of process options or consider all economic, technological, institutional, legal or other factors affecting implementation of these changes. Instead we have relied on our own background experience, industry contacts, and the guidance of the Project Officer and EPA advisors to choose the following processes (or process elements) for consideration in the chlor-alkali industry:

- dimensionally stable anodes - conventional and expandable,
- diaphragm cell synthetic membrane,
- mercury cell,
- power recovery from sodium-mercury amalgam,

- regeneration of chlorine from spent hydrogen chloride,
- production of caustic soda from soda ash,
- bi-polar electrolytic cells,
- multi-effect evaporation, and
- natural versus synthetic soda ash.

From this listing, we chose the first three for detailed analyses, because the options or modifications are considered to be the most likely to have a significant impact on overall energy consumption in the chlor-alkali industry over the next five to ten years. The other six options either have relatively small energy consequences and would therefore be implemented for other reasons, or have important shortcomings as substitutes for current technology.

II. FINDINGS, CONCLUSIONS, AND RECOMMENDATIONS

The chlor-alkali industry is large, mature, and growing at a rate averaging 5-6% per year. Since the plants are long-lived and the rate of equipment renewal is low, changes are implemented gradually and considerable time passes before a significant portion of industry capacity is affected by change.

During the next 15 years the following evolutionary changes in the industry are expected, in approximately the order listed:

- Existing graphite anode plants will be converted to dimensionally stable anode (DSA) cells,
- Deposited asbestos diaphragms will be replaced with stabilized asbestos diaphragms,
- New plants will use combinations of expandable DSA type cells or wide DSA's with stabilized asbestos diaphragms,
- Microporous membranes will supersede the use of asbestos in new plants and probably be used for some existing plant modernizations,
- Mercury cells, which expose the industry to considerable risk in the form of plant maloperation or accidents and which use more energy (combining both electrical and thermal forms) than the newest DSA/ modified diaphragm cells, will be slowly phased out over the next ten years, and
- Perfection of the ion exchange membrane cell will enable it to economically replace mercury cells in existing mercury cell plants.

The effect of these changes will be a reduction of 15% or more in the average energy consumed by the industry per ton of product. Although the present environmental problems of the industry, with the exception of mercury cell plants, are comparatively minor, these changes will ease existing problems as shown in summarized form in Table II-1. The already small volume of chlorinated organic waste associated with the use of graphite anodes will be eliminated, as will the solid graphite waste from spent anodes. Traces of lead in wastewater arising from the lead used to set the graphite will also be eliminated. Stabilized asbestos diaphragms will greatly reduce solid asbestos waste from spent diaphragms and essentially eliminate asbestos fibers in wastewater. Polymer membranes, either microporous or ion exchange, will eliminate all asbestos from the plant. Higher purity cell gas from DSA cells reduces the amount of gas necessarily vented from the chlorine liquefaction system.

TABLE II-1

COMPARISON OF BASE LINE AND ALTERNATIVE PROCESSES

	Base Case	Process Changes				Modern Mercury Cell*
Cell Anode Cell Cathode Diaphragm	Graphite Deposited Asbestos	Standard DSA Deposited Asbestos	Wide DSA Stabilized Asbestos	DSA Microporous Membrane	DSA Ion Exchange Membrane	DSA Hg
Environmental Factors						
Pollution Control Costs ($/Ton of Chlorine)	0.64	0.55	0.55	0.50	0.50	3.60
Comments		Waste graphite and chlorinated hydrocarbons eliminated, reduced tail gas volume. Lead effluent eliminated.	Same as Std DSA but waste asbestos easier to remove from effluent.	Same as Std DSA but asbestos eliminated from process.	Same as DSA - microporous membrane plus elimination of inorganic salt purge from evaporator section.	
Energy Factors						
Consumption per Ton of Product						
Electrical kWh	3274	3151	2826	2826	3363	3716
Fuel 10^6 Btu	6.21	5.01	5.01	5.01	0.91	0.56
Total 10^6 Btu	40.58	38.10	34.68	34.68	36.22	39.53
Comments		Improved electrode reduces resistance losses and over-voltage effects.	Closer electrode spacing reduces resistance losses.	Same as wide DSA.	Production of high strength caustic in cell increases power use, reduces fuel use.	
Process Economics						
Fixed Investment (10^6 $)	56.4	54.2	54.5	54.5	57.2	58.20
Pollution Control and Operating Costs ($/Ton of Chlorine)	116.01	107.65	104.03	103.53	109.38	138.08

*Although this is not a process change in the same sense as the others displayed on this table, it was discussed in this report and is therefore included in this summary table.

Source: Arthur D. Little, Inc., estimates and industry data.

In summary, none of these process changes in themselves are expected to create new environmental problems. On the contrary, the changes are expected to further reduce the amount of pollution generated by the industry. Consequently, it is recommended that any research, development, or demonstrations effort be oriented toward accelerating and evaluating the introduction of the newer, less polluting, and energy conserving technology.

III. INDUSTRY OVERVIEW

A. DESCRIPTION

In terms of both production volume and level of energy consumption, the most important segment of the U.S. chlor-alkali industry consists of some 30 manufacturers (see Tables III-1 and III-2) who electrolyze crude salt brine to form sodium hydroxide (caustic soda, or caustic) and chlorine. Chlorine and caustic are coproducts, with about 1.1 tons of caustic soda (100 percent basis) produced for each ton of chlorine. Of the 11 million short tons of chlorine produced in the United States in 1974, over 95% was made with caustic soda as the coproduct. The balance was produced as a coproduct of potassium hydroxide, or sodium metal, or was regenerated from byproduct hydrogen chloride. Because it is difficult to store large quantities of chlorine except in the form of end products, the production of caustic soda is closely tied to the demand for chlorine.

TABLE III-1

U.S. CHLORINE PRODUCERS AND CAPACITIES
(short tons per day - 1974)

Producer	Capacity
Alcoa	470
Allied	1,650
BASF Wyandotte	1,550
Diamond Shamrock	3,200
Dow	11,000
DuPont	940
Ethyl	640
FMC	790
Goodrich	300
Hooker	2,680
Kaiser	535
Linden Chlorine	460
Mobay	200
Monsanto	250
Olin	1,625
Pennwalt	950
PPG	3,330
Shell	375
Sobin	310
Stauffer	980
Vulcan	375
Paper Companies	690
Other	1,180
TOTAL	34,480

Source: Chemical Profiles, Schnell Publishing Co., New York.

TABLE III-2

U.S. CAUSTIC SODA PRODUCERS AND CAPACITIES
(short tons per day - 1974)

Producer	Capacity
Alcoa	520
Allied	1,760
BASF Wyandotte	1,780
Diamond Shamrock	3,420
Dow	12,000
Ethyl	200
FMC	860
Linden Chloride	510
Goodrich	330
Hooker	2,840
Kaiser	590
Monsanto	275
Olin	1,820
Pennwalt	935
PPG Industries	3,660
Shell	410
Sobin	340
Stauffer	1,080
Vulcan	445
Paper Companies	760
Other	510
TOTAL	35,045

Source: Chemical Profiles, Schnell Publishing Co., New York.

Approximately 75% of U.S. chlorine is used in the production of other chemical products, the most important of which are vinyl chloride plastics, chlorinated solvents, and fluorocarbons. That portion of chlorine not used as a raw material is used chiefly in the pulp and paper industries and in water treatment (see Table III-3). Of the 10 million tons of caustic soda consumed in the United States in 1974, nearly 85% was used by various sectors of the chemical and allied products industry. Among the most important uses of caustic are those in pulp and paper processing, the production of miscellaneous organic chemicals, and neutralization of spent acid wastes in several industry sectors (see Table III-4).

1. Industry Sectors

Broadly defined, the U.S. chlor-alkali industry includes manufacturers not only of chlorine and caustic, but also of sodium carbonate (soda ash), sodium bicarbonate, and caustic potash. The latter three chemicals are not treated in detail in this study, either because of their small production volume (sodium bicarbonate and caustic potash represented less than 1% of total chlor-alkali shipment in 1974), or because changes in energy requirements associated with expected changes in technology are small and decreasing relative to chlorine and and caustic soda (such as in the case of soda ash).*

TABLE III-3

1974 U.S. CHLORINE DEMAND PATTERN

	Thousands of of short tons	Percent
ORGANIC CHEMICALS		
One-Carbon Compounds	1,620	15
Two-Carbon Compounds	3,220	29
Three-Carbon and Above	600	6
Cyclic Compounds	510	5
Oxygen-Containing Compounds	1,120	10
SUBTOTAL	7,070	65
NON-ORGANIC		
Inorganic Chemicals	1,270	12
Pulp & Paper	1,460	13
Water Treatment	540	5
SUBTOTAL	3,270	30
TOTAL DEMAND (includes unspecified)	10,930	100

Source: Arthur D. Little, Inc. estimates, based on industry contacts.

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*The replacement of synthetic soda ash facilities with natural soda ash facilities results in nearly a 50% reduction in process energy requirements per unit of production. (We have not included consideration of energy requirements for delivery of the product to major markets because transportation aspects were specifically excluded from the scope of this study.)

TABLE III-4

1974 U.S. CAUSTIC SODA DEMAND PATTERN

	Thousands of short tons, 100 percent NaOH	Percent
INORGANIC CHEMICALS		
Brine Treatment	294	
Alumina	515	
Sodium Hypochlorite	241	
SUBTOTAL	1,050	10
ORGANIC CHEMICALS		
Phenols & Dyes	535	
Caustic Scrubbing	590	
Neutralization	1,333	
Misc. Organics	1,996	
SUBTOTAL	4,545	41
CELLULOSE PROCESSING		
Pulp & Paper	2,177	
Rayon	309	
Cellophane	238	
SUBTOTAL	2,724	25
SOAP & CLEANERS	600	6
PETROLEUM REFINING	352	3
MISC. & UNIDENTIFIED	629	6
TOTAL DOMESTIC DEMAND	9,809	
NET EXPORTS	1,019	9
TOTAL DEMAND	10,828	100

Source: Arthur D. Little, Inc., estimates, based on industry contacts.

In terms of 1974 production volume, chlorine and caustic accounted for approximately 80% of chlor-alkali industry production. Estimated 1974 shipment value was approximately $1 billion, with an estimated 13,000 workers (see Table III-5).

In 1967, synthetic soda ash production accounted for nearly 75% of total soda ash output. Since then, pollution problems have resulted in the closure of some synthetic soda ash plants and the construction of several natural soda ash plants in Wyoming and California. In 1974, production of natural soda ash exceeded production of synthetic soda ash; by 1980, new and expanded natural soda ash facilities are expected to provide about 75% of total output.

Producers of chlorine and caustic may be segmented on the basis of production process. Approximately 70% of U.S. chlorine and caustic production is via the diaphragm cell; approximately 25% via the mercury cell; and 5% via the Down's cell or as a byproduct in the manufacture of magnesium, potassium hydroxide, and potassium nitrate. The technology for both mercury and diaphragm cells was developed in the United States in the 1890's and, although many refinements have been made to increase efficiency and reduce pollution, the technology has remained basically the same. Both cells produce comparable grades of chlorine, but the mercury cell produces a more concentrated caustic solution of higher purity than that obtained from the diaphragm cell. A comparison of energy consumption by the two cells is complicated by the fact that the mercury cell requires more electrochemical energy but less heat (for evaporation) to produce a commercial concentration of aqueous caustic soda.* Although both cells contribute to environmental pollution in various ways, the 1970 discovery of mercury in fish gave rise to considerable concern over continued use of mercury cell technology. This concern has already lead to a 90% reduction in mercury effluents, but contamination of the environment by mercury and other heavy metals remains a matter of concern.

Non-electrolytic chlorine production, such as by the Kel-Chlor® process, is a small but growing source of the chemical. The process, however, does not represent alternative technology for the electrolytic process, because the chlorine output represents "recycled" chlorine which is generally being recovered from a waste stream of HCl. In addition, non-electrolytic chlorine production produces no coproduct caustic soda and the demand for caustic would need to be met by an additional, independent process.

2. Plant Characteristics

A summary of statistical information relating to the number, age, size and location of U.S. chlor-alkali plants is presented in Appendix A. In 1972 (the last year for which detailed information is available), a total of 67 establishments produced chlorine, while 59 produced caustic.

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*Details of this comparison are presented in Chapter IV.

TABLE III-5

CHLOR-ALKALI INDUSTRY: TRENDS AND PROJECTIONS 1967-75[1]

(In millions of dollars except as noted)

	1967	1970	1971	1972	1973[2]	1974[2]	Percent Increase 1973-74	1975[2]	Percent Increase 1974-75
Industry:[3]									
Value of shipments	720	660	676	803	841	1,000	19	1,130	13
Total employment (000)	19	15	14	13	13	13	0	14	8
Production workers (000)	13	11	10	10	10	10	0	11	10
Value added	419	362	360	437	---	-----	--	-----	--
Value added per production worker man-hour ($)	16.44	16.91	18.38	23.10	---	-----	--	-----	--
Product:[4]									
Value of shipments	623	638	706	801	821	975	19	1,100	13
Value of imports	6	5	7	9	14	18	29	22	22
Value of exports	36	55	73	81	79	108	37	125	16
Production (000 short tons)									
Sodium carbonate, synthetic	4,849	4,393	4,128	4,310	3,838	3,600	-6	3,700	3
Chlorine gas[5]	7,680	9,710	9,317	9,873	10,302	11,000	7	11,600	5
Chlorine, liquid	3,936	4,521	4,571	4,919	5,200	5,600	8	5,900	5
Caustic soda, liquid	7,690	9,382	9,074	9,583	10,250	11,600	13	11,800	2
Caustic soda, dry	565	564	544	475	459	500	9	525	5
Sodium bicarbonate	122	143	121	122	125	125	0	130	4
Caustic potash	175	175	186	176	188	190	1	192	1

[1] Does not include natural soda ash.

[2] Estimated by Bureau of Domestic Commerce (BDC).

[3] Value of all products and services sold by the Chlor-Alkali Industry (SIC 2812).

[4] Value of shipments of chlor-alkalies made by all industries.

[5] Includes quantities converted to liquid.

n.a. = Not available.

Source: U.S. Industrial Outlook 1975, U.S. Department of Commerce, Bureau of Domestic Commerce, from Bureau of the Census, Bureau of Labor Statistics, BDC.

Approximately 60% of U.S. chlorine and caustic plants are 5 to 30 years old. Approximately 10% are less than 5 years old, while approximately 30% are more than 30 years old. In terms of production volume, plants built within the last five years account for a proportionately larger share of total production, because of their much larger size.

Plant sizes vary from as little as 10 tons per day for older plants, up to 1200 tons per day for plants built in the 1970's. The average plant size (1974) is approximately 900 tons per day.

The distribution of plant locations is heavily weighted toward the states of Texas (with 12) and Louisiana (with 10). Together, these two states account for about 60% of U.S. chlorine production. Other states having more than three chlor-alkali establishments are Alabama and Michigan, New York, Ohio, and Washington. As may be expected, the largest plants tend to be located in those states having the greatest number of plants.

Plant distribution by process is detailed in Appendix A. A review of this information shows that the highest concentration of mercury cells is in Alabama, Louisiana, and New York, while the highest concentration of diaphragm cells is in Louisiana, Michigan, and Texas.

3. Type of Integration

The U.S. chlor-alkali industry exhibits characteristics of both vertical and horizontal integration to varying degrees -- generally in proportion to the overall size of the producing companies. Although the degree of integration varies widely from company to company, in terms of vertical integration, the average company in the industry consumes captively approximately 60% of its production. In terms of horizontal integration, the average company depends on chlor-alkali products for approximately 10-15% of its sales. These average figures may be misleading, because captive consumption may reach 100% in some cases and horizontal imtegration may be nonexistent in other cases.

B. ECONOMIC OUTLOOK

Although several serious threats to future chlorine demand can be identified, the long-range prospects for the U.S. chlor-alkali industry appear to be reasonably favorable.

1. Historical Trends and Projected Growth

Historical levels of U.S. production, trade, and apparent consumption of chlorine, caustic and soda ash are presented in Tables III-6, III-7 and III-8. U.S. chlorine production volume has traditionally reflected the performance of the U.S. economy. On the basis of a healthy economy between 1955 and 1968, apparent U.S. consumption of chlorine grew at an average annual rate of 6.3% during the period. However, since 1968, because of the economic slowdown of 1970-71 and recent capacity constraints, annual chlorine consumption increases have averaged only 4.3%. With the addition of significant new industry capacity in late 1974 and early 1975, U.S.

TABLE III-6

U.S. CHLORINE PRODUCTION, TRADE, AND APPARENT CONSUMPTION, 1955-74
(Millions of Short Tons)

Year	Production	Imports	Exports	Apparent Consumption
1955	3.42	0.01	0.04	3.39
1956	3.79	0.02	0.04	3.77
1957	3.95	0.01	0.04	3.92
1958	3.60	0.01	0.03	3.58
1959	4.35	0.02	0.03	4.34
1960	4.64	0.03	0.03	4.64
1961	4.60	0.02	0.03	4.59
1962	5.14	0.03	0.04	5.13
1963	5.46	0.02	0.04	5.44
1964	5.95	0.02	0.04	5.93
1965	6.52	0.04	0.04	6.52
1966	7.20	0.07	0.02	7.25
1967	7.68	0.06	0.04	7.70
1968	8.44	0.04	0.04	8.44
1969	9.38	0.03	0.03	9.38
1970	9.76	0.03	0.02	9.77
1971	9.35	0.04	0.01	9.38
1972	9.87	0.04	0.01	9.90
1973	10.30	0.05	0.01	10.34
1974	10.62	0.08	0.02	10.68

Source: Production from U.S. Department of Commerce, Current Industrial Reports Series M28A, and Import and Export Statistics from U.S. Department of Commerce, FT110, FT125,FT410.

TABLE III-7

U.S. CAUSTIC SODA PRODUCTION, TRADE, AND APPARENT CONSUMPTION, 1955-74
(Millions of Short Tons)

Year	Production	Imports	Exports	Apparent Consumption
1955	3.915	small	0.228	3.687
1956	4.227	small	0.264	3.963
1957	4.336	small	0.291	4.045
1958	3.993	0.004	0.209	3.788
1959	4.748	0.002	0.247	4.503
1960	4.972	0.002	0.239	4.735
1961	4.914	small	0.228	4.686
1962	5.486	small	0.202	5.284
1963	5.814	small	0.321	5.493
1964	6.389	0.001	0.496	5.894
1965	6.831	0.003	0.420	6.414
1966	7.596	0.009	0.430	7.175
1967	8.398	0.018	0.565	7.851
1968	8.868	0.039	0.646	8.261
1969	9.917	0.040	0.814	9.143
1970	10.141	0.063	1.062	9.142
1971	9.667	0.076	1.216	8.527
1972	10.270	0.105	1.202	9.172
1973	10.541	0.135	1.034	9.779
1974	10.87	0.12	1.14	9.85

Source: Production from U.S. Department of Commerce, Current Industrial Reports Series M28A, and Import and Export Statistics from U.S. Department of Commerce, FT110, FT125, FT410.

TABLE III-8

U.S. SODA ASH PRODUCTION, TRADE, AND APPARENT CONSUMPTION, 1955-74
(Millions of Short Tons, 100% Na_2CO_3)

	Production					
Year	Synthetic	Natural	Total	Imports	Exports	Apparent Consumption
1955	4.907	.689	5.596	Neg.	.185	5.413
1956	4.998	.655	5.653	Neg.	.225	5.376
1957	4.659	.677	5.336	Neg.	.178	5.121
1958	4.324	.627	4.951	Neg.	.128	4.845
1959	4.904	.715	5.619	Neg.	.173	5.462
1960	4.558	.790	5.348	Neg.	.170	5.163
1961	4.516	.785	5.301	Neg.	.140	5.197
1962	4.607	.978	5.601	Neg.	.152	5.403
1963	4.682	1.119	5.797	Neg.	.184	5.627
1964	4.948	1.275	6.223	Neg.	.276	5.920
1965	4.926	1.494	6.420	Neg.	.277	6.179
1966	5.071	1.738	6.809	Neg.	.346	6.548
1967	4.849	1.748	6.597	Neg.	.304	6.244
1968	4.596	2.043	6.639	Neg.	.288	6.463
1969	4.540	2.513	7.053	Neg.	.324	6.688
1970	4.393	2.688	7.081	Neg.	.336	6.753
1971	4.298	2.857	7.155	Neg.	.437	6.747
1972	4.310	3.129	7.439	Neg.	.480	6.947
1973	3.838	3.632	7.470	Neg.	.425	7.008
1974	3.503	4.030	7.533	.035	.552	7.016

Source: Production from U.S. Department of Commerce, Current Industrial Reports series M28A, and Import and Export statistics from U.S. Department of Commerce, FT110, FT125, FT410.

chlorine production should not be capacity-constrained in the foreseeable future. Between 1974 and 1980 U.S. chlorine demand is expected to grow at an average annual rate of about 5%, bringing total 1980 demand to a level of approximately 15 million tons.

Historic demand growth for caustic soda has been somewhat below that of chlorine, averaging about 5.3% since 1955. Growth in demand for caustic is typically less affected by economic factors than is that of chlorine. However, because the production of caustic soda is closely tied to chlorine production, its supply is a function of chlorine demand levels. This relationship has lead to situations of both over- and under-supply as the demand for chlorine has fluctuated above and below demand for caustic. In the most recent economic slowdown (1974/75), drastically reduced levels of chlorine demand led to extreme tightness in domestic caustic soda markets. Future U.S. demand growth for caustic is expected to be at an average annual rate greater than 5%. Total U.S. apparent consumption in 1980 is forecast at approximately 15 million tons.

The rate of demand growth for soda ash has been the lowest of the three major chlor-alkali chemicals. Demand for caustic shows little correlation with the U.S. economy. As shown in Table III-8, domestic apparent consumption has grown at an average rate of only about 1.5% per annum since 1955. This slow rate of growth is due in part to the replacement of soda ash by caustic soda in some applications. Assuming a continuation of the current strong demand for soda ash by glass manufacturers, the outlook for domestic consumption is for continued slow growth but at a more rapid average rate of 2.5 to 3% per annum. The more rapid growth rate to 1980 is also a reflection of slower loss of markets to caustic soda. Estimated 1980 U.S. consumption will be approximately 8 million tons.

2. Technical and Economic Life of Manufacturing Facilities

As already indicated, nearly 30% of U.S. chlorine plants are more than 30 years old and are still using essentially the same technology as was developed near the turn of the century. However, plants that are this old have been rebuilt in almost every case, because average cell life is on the order of 20 years. Even without rebuilding, a 5% average annual growth implies that half of industry capacity existing in 1990 will have been built after 1975.

IV. COMPARISON OF CURRENT AND ALTERNATIVE PROCESSES

A. BASIS FOR SELECTING PROCESSES

The caustic-chlorine industry in the United States is a large, mature part of the chemical industry with 34,000 tons per day of installed chlorine capacity as of January 1975. All but 5.3% of this capacity is represented by salt brine electrolysis plants, with diaphragm cells accounting for 69.9% and mercury cells 24.8%. The size and maturity of the industry result in process changes being evolutionary, rather than radical, and in a rather long time being required before process changes or alternative processes have a significant impact on the entire industry.

Over the history of the industry, process changes have been primarily those that reduce cost by improving energy efficiency. The energy intensity of the electrolytic processes has always made power cost a major expense, and has promoted efforts to mitigate very high capital intensity by developing larger and more efficient cells and plants. Current large increases in the cost of energy have provided a major impetus to accelerate development of energy-reducing techniques. However, from our knowledge of the industry, and through discussions with the major companies in the industry, we believe that most of the process changes to be implemented during the next five years will consist of incremental energy-saving techniques rather than radical step changes.

To focus our efforts on the most likely changes in the industry, we selected the following for detailed analysis:

- The use of dimensionally stable anodes (DSA) to replace graphite anodes; and
- The use of modified diaphragms to provide improved cell electrical characteristics and permit a more concentrated caustic to be produced, with reduced energy for evaporation.

There are several variations of these two categories, which we have analyzed to assess their probable degree of implementation.

As was mentioned before, the mercury cell process accounts for about 25% of present chlorine production but, because of environmental problems associated with mercury, its use is declining.* To help determine whether or not research to improve the environmental aspects of the mercury cell process is desirable (as it certainly would be if the process used less energy), we compared the relative energy consumption of that process with the diaphragm cell process.

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*For most plants, the industry rapidly developed techniques to comply with EPA requirements at acceptable cost levels, but there has been considerable difficulty in complying, on a constant and affordable basis, with OSHA regulations. In addition to plant changes, compliance with OSHA regulations involves drastic changes in employee assignments and work habits which are difficult for management to enforce.

B. COMPARISON OF PRESENT PROCESS WITH ALTERNATIVES

1. Base Line Process - Graphite Anode Diaphragm Cell

We selected the graphite anode diaphragm cell process as a basis for judging the energy and environmental effects resulting from process changes. The diaphragm process represents over 65% of U.S. chlorine capacity and, even though conversion to the use of dimensionally stable anodes is rapidly taking place, the graphite anode version of the process is still a basis of industry comparison.

Although not used as a basis for comparison, the mercury cell process is fully discussed later in this section. The waste effluent aspects of both processes are also presented.

a. Process Description

As shown schematically in Figure IV-1, the major raw material for the diaphragm cell process is a nearly saturated solution of sodium chloride made up by dissolving purchased solid salt in water or brine, or (much more commonly in the U.S.) by injecting water into an underground salt structure. The crude brine must be purified before it is suitable for use as a feed to the cells. This is carried out by adding sodium carbonate, often produced at the plant by treating cell liquor with flue gas, and dilute caustic soda (cell liquor) to raise the pH to 10 or 11. Heavy metals and magnesium are precipitated as hydroxides and calcium as the carbonate. A flocculating and settling aid is usually added to aid in the settling of the precipitates which are then filtered from the brine. The waste sludge is generally sent to a lagoon. This stream and other wastes are described in Table IV-1. The brine is then heated and brought to saturation by the addition of pure salt recycled from the caustic evaporator system. The pH is adjusted to about 6 with hydrochloric acid to remove excess alkalinity, which would form hypochlorites and chlorates in the cell, before the brine is introduced to the electrolytic cells.

In the cells the brine is electrolyzed to produce chlorine, caustic soda and hydrogen:

$$2\ NaCl + 2\ H_2O \rightarrow Cl_2 + 2\ NaOH + H_2$$

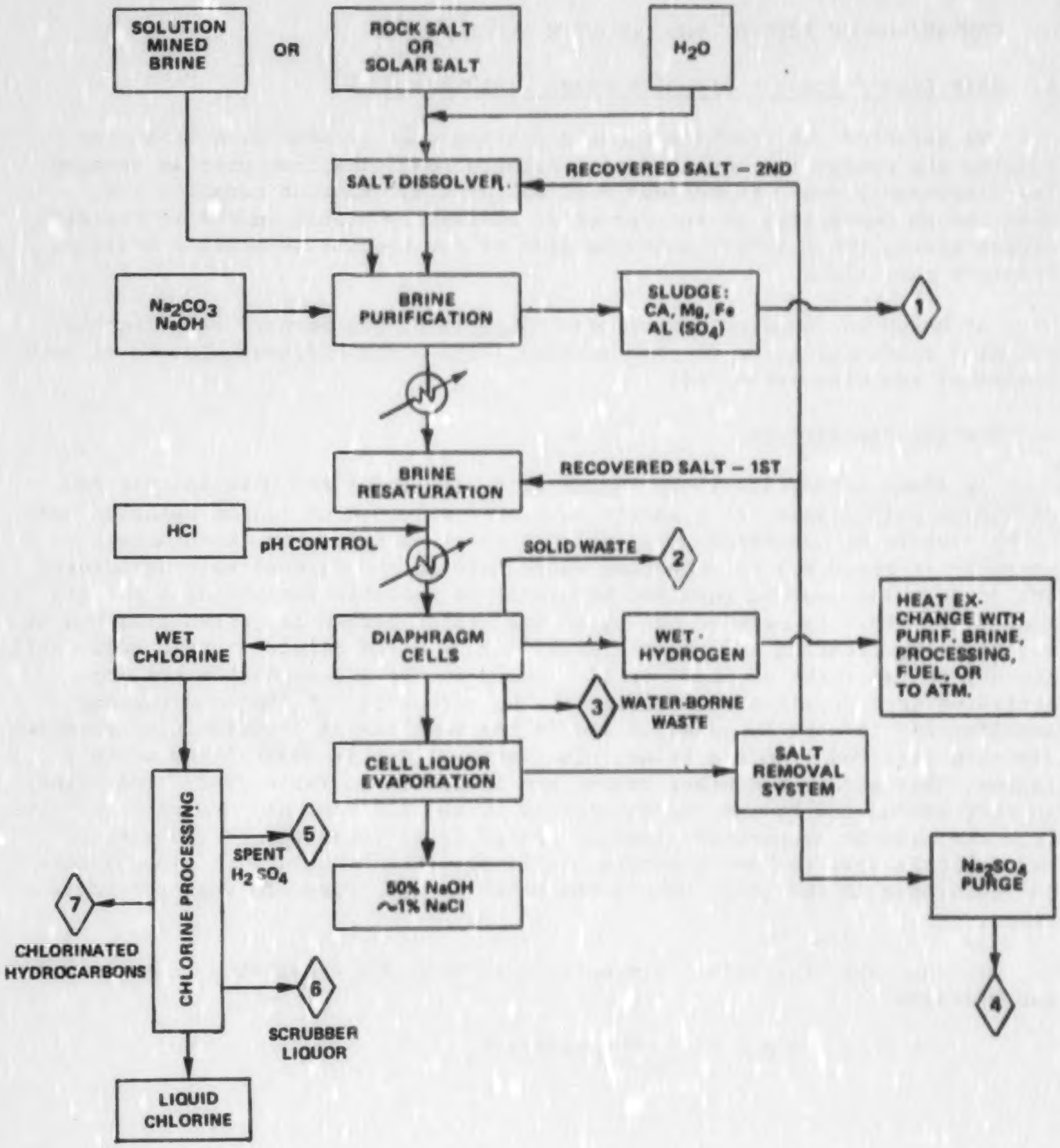
SOLUTION MINED BRINE
OR
ROCK SALT OR SOLAR SALT
H_2O
SALT DISSOLVER
RECOVERED SALT – 2ND
Na_2CO_3 NaOH
BRINE PURIFICATION
SLUDGE: CA, Mg, Fe AL (SO_4)
1
BRINE RESATURATION
RECOVERED SALT – 1ST
HCl
pH CONTROL
SOLID WASTE
2
HEAT EX-CHANGE WITH PURIF. BRINE, PROCESSING, FUEL, OR TO ATM.
WET CHLORINE
DIAPHRAGM CELLS
WET HYDROGEN
3
WATER-BORNE WASTE
CELL LIQUOR EVAPORATION
SALT REMOVAL SYSTEM
CHLORINE PROCESSING
5
SPENT H_2SO_4
50% NaOH ~1% NaCl
Na_2SO_4 PURGE
7
CHLORINATED HYDROCARBONS
6
SCRUBBER LIQUOR
4
LIQUID CHLORINE

Figure IV-1. Diaphragm Cell Process

TABLE IV-1

WASTE STREAMS FROM DIAPHRAGM CELL PROCESS

Stream	Source and Comments	Components	Quantity lbs/1000 lb Cl_2	Normal Disposition
1	Sludges from brine purification, amount & nature depends upon salt purity	$Mg(OH)_2$		Sent to lagoon
		$CaCO_3$		
		Iron & other metal hydroxides		
		Total	15	
		Filter Aid	0.2	
		NaCl	3	
		Water	45	
2	Materials from rebuilding electrolytic cells	Concrete & graphite rubble	3	Landfill dump
		Asbestos fibers	0.4	
3	Housekeeping operations, equipment cleaning	NaCl	50	Sent to lagoon or severed
		NaOH	5	
		Lead	0.04	
		Copper	< 0.01	
		Water, approx.	600	
4	Recycled salt from evaporators is washed to dissolve sodium sulfate so that it can be purged	Na_2SO_4	10	Sent to lagoon or neutralized and put into receiving water where allowable
		NaOH	20	
		NaCl	50	
		Water, approx.	150	
5	Diluted sulfuric acid from chlorine drying towers	H_2SO_4, 93 to 70%	35 to 10	Sold for use or for reconcentration
6	Final vent scrubber after normal removal of chlorine from tail gas and other vents. Dilute caustic soda used as absorbent.	NaOCl	1	Sent to lagoon or severed
		$NaHCO_3$	3	
		Water, approx.	40	
7	Product chlorine purification	Chlorinated organics of unspecified nature	0.45	Drummed for disposal by incineration or landfill

Source: Arthur D. Little, Inc., estimates and "Assessment of Industrial Hazardous Waste Practices, Inorganic Chemicals Industry," U.S. Environmental Protection Agency, Contract 68-01-2246, 1975.

Chlorine is formed at the graphite anode, bubbles to the top of the cell, and is removed by the chlorine header. The cathode is a hollow plate made of iron mesh with a deposited asbestos layer, or diaphragm on the outside. The sodium ion migrates to the cathode where hydroxyl ion and hydrogen are formed:

$$2Na^+ + 2H_2O + 2e^- \rightarrow H_2 + 2OH^- + 2Na^+$$

Thus, a solution containing 10-11% NaOH is generated in the cathode compartment.

The purpose of the diaphragm is to hinder back-migration of hydroxyl ions to the anode area where they would react with the chlorine, ultimately forming chlorates and thereby reducing cell current efficiency.

The hydrogen from the top of the cathode is piped from the cells, cooled to remove water and then, depending on circumstances, burned for fuel, sold, or flared. The disposition of the hydrogen depends on specific local conditions. If a local industrial gas market exists, the hydrogen is often sold to a company for purification, bottling, and distribution. Large plants can economically install the added equipment for the safe burning of hydrogen (up to about 50% of total fuel), in the steam boiler, or can use it as a chemical synthesis material. Of course, the latter use involves entering a new business with major capital expenditures. Small operators, as well as many intermediate sized plants, must vent the hydrogen, either entirely or that in excess of possible sales.

The cell liquor withdrawn from the cathode still contains about 13-15% salt, because only 50% of the salt is decomposed at optimum cell operating conditions. This liquor is concentrated in steam-heated, multi-effect evaporators (usually triple effect) to produce a 50% caustic soda product which contains about 1% salt. The remaining salt crystallizes out during concentration and is centrifuged from the caustic and recycled for brine saturation.

For those very few applications which require a "salt-free" caustic, such as rayon, diaphragm cell caustic can be purified by any one of several proven techniques. The most common is an anhydrous ammonia extraction process which removes chlorates and a number of other minor inorganic salt impurities along with the sodium chloride.

To control the buildup of sulfate ions in the salt recycle (introduced as one of the major impurities in the feed salt or brine) and thus in the brine system, a small purge stream is taken at the point of maximum sulfate concentration. Where allowable this stream, after neutralization, is sewered or put into a river or ocean. If such disposal is not allowable it is lagooned.

The wet chlorine from the cells is cooled to remove water, dried in sulfuric acid scrubbers, then compressed and liquefied. The presence of small amounts of air (in-leaks from the chlorine duct system) and other inert gases results in a residual gas containing about 35% Cl_2 after liquefaction. This tail, or blow gas, can be used to make bleach or burned to form hydrogen chloride. Systems for its recovery as chlorine are also available.

In the chlorine drying towers 98-104% sulfuric acid (or oleum) is used in a countercurrent fashion to remove water vapor from the chlorine. The spent acid from the first tower is about 70% H_2SO_4 and the disposal technique used depends on specific conditions at the site. It is often returned to processors for refortification, or sold for uses such as fertilizer manufacture that can use a dilute, impure acid. Only in unusual instances must it be wasted by neutralization and lagooning.

In the cells, the graphite anodes are gradually consumed by side reactions involving oxygenated compounds which form carbon monoxide by reaction with the graphite and by chemical attack on the organic binder. The graphite particles which are formed tend to clog the diaphragm on the cathode. Both of these effects increase the electrical resistance of the cell. As the graphite is consumed, the surface area of the anode decreases, increasing current density, and its distance from the cathode increases. As the diaphragm is plugged its electrical resistance, as a result of decreased ion passage, increases. Thus power consumption per ton of product gradually increases and at some point the cell is removed from the circuit and rebuilt. The debris from cell rebuilding, asbestos diaphragm material, anode stubs, and concrete cell bodies is disposed of through landfill dumping.

The reactions between chlorine and the organic materials in the graphite anode lead to the formation of volatile chlorinated organic materials of rather indefinite composition. Thus, in addition to the problems associated with physical disintegration of the anode, the chemical attack produces impurities in the chlorine which must be removed and safely treated for disposal, generally by incineration with acid fume absorption or by acceptable landfill operations.

b. Cost of Production

Based on a modern large plant with a capacity of 1000 tons of chlorine per stream day, the cost of production is estimated to be \$84.04 per ton of chlorine, as shown in Table IV-2. Coproduced with this chlorine would be 1.055 tons of caustic soda per ton of chlorine, or 380,000 tons/year. As is normal in the industry, in this estimate all costs are placed on chlorine, or as it is often expressed, the costs are on an electrochemical unit (ECU) basis. The ECU is one ton of chlorine plus the coproduced caustic, or in this case 2.055 tons of product. This estimate is based on 360 stream days per year, normal for the industry, and current costs for labor and materials on the U.S. Gulf Coast.

To the production cost, which includes depreciation on an 11-year straight-line basis, we have added an amount equal to 20% of the fixed investment to allow for a minimum pre-tax return, or \$31.33/ton, and pollution control cost of \$0.64/ton to arrive at a total of \$116.01 per ton of chlorine or ECU.

TABLE IV-2

ESTIMATED PRODUCTION COST OF CHLORINE AND CAUSTIC SODA

Process: Electrolysis of Brine, Graphite Anode Diaphragm Cell
Annual Production: 360,000 Tons Chlorine
380,000 Tons Caustic Soda (100% basis as 50%)
Stream Days/Year: 360
Plant Location: U.S. Gulf Coast
Depreciation Period: 11 years (IRS Guideline)
Fixed Investment: $56,400,000

	Units Used or Annual Basis	$/Unit	Units/Ton of Chlorine	$/T Cl_2
Variable Costs				
Salt (100% as brine)	tons	2.00	1.75	3.50
Misc. Chemicals	-	0.80	1.0	0.80
Graphite Anodes	pounds	0.80	7.0	5.60
Diaphragm Material	-	0.20	1.0	0.20
Cell Rebuilding Supplies	-	0.75	1.0	0.75
Power	kWh	0.012	3274.0	39.29
Fuel for Steam (Gas)	10^6 Btu	0.70	9.15	6.40
H_2 Fuel Credit	10^6 Btu	0.70	2.94	(2.06)
Cooling Water Circ.	10^3 gal	0.02	40.0	0.80
Process Water	10^3 gal	0.25	1.9	0.48
				55.76
Semi-Variable Costs				
Operating Labor	42 men	12,000/yr		1.40
Supervision	8 foremen	18,000/yr		0.40
	1 superintendent	25,000/yr		0.07
Labor Overhead	35% of Labor & Supervision			0.66
Maintenance	5% of Investment			7.83
				10.36
Fixed Costs				
Plant Overhead	70% of Labor & Supervision			1.31
Local Taxes & Insurance	1.5% of Investment			2.35
Depreciation	9.0% of Investment			14.26
				17.92
TOTAL PRODUCTION COSTS				84.04
Return on Investment (Pretax)	20% of Investment			31.33
Pollution Control	See Table IV-5			0.64
TOTAL				116.01

Source: Arthur D. Little, Inc. estimate

The total estimated fixed investment is \$56.4 million, including the process units themselves and all necessary auxiliary facilities. Power generation is not included. (The capital investment for pollution control is estimated to be \$355,000 as described later in Chapter IV, Section 3.2, Table IV-5.)

We assumed that plant location allows solution mining of an underground salt bed resulting in a unit cost of \$2.00 per ton of salt. Purchased solid salt would be much more expensive, about \$12.00/ton delivered.

c. Energy Usage

Energy costs, both power at 1.2¢/kWh (utility company published rates show ranges of 1.05 to 1.4¢/kWh at Gulf Coast locations for large loads) and net fuel at 70¢/10^6 Btu account for about 45% of total cost, which indicates why the industry is concentrating on process research to reduce energy consumption.

The electrical energy use in the plant, 3274 kWh per ton of chlorine, is almost entirely used for cell electrolysis as shown in the following:

	kWh/ton chlorine
DC Power to Cell	2894
Busbar Losses	30
Total DC Power	2924
AC Power at 97% Efficiency*	3014
Chlorine Liquefaction & General Plant	250
Auxiliary Power	10
Total AC Power	3274
Added power for environmental control	0.23 (Negligible)

In addition to this energy usage, the plant requires the following amounts of steam:

	lb/ton chlorine
Caustic Evaporation	6368
Brine Heating and Misc.	700
	7368

Based upon 1100 Btu/lb of low-pressure steam and an 85% boiler efficiency, the fuel requirement is 9.15 x 10^6 Btu/ton of chlorine.

As mentioned, hydrogen is produced at the cell cathode at the rate of 10.7 x 10^3 SCF/ton of chlorine. Using a lower heating value of 275 Btu/SCF the heating value of this hydrogen is 2.94 x 10^6 Btu/ton of chlorine, so that the net fuel requirements decrease to 6.21 x 10^6 Btu/ton. The lower heating value is used since, particularly for hydrogen, it is a better measure of useful heat than is the higher heating value.

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*3% transformer and rectifier losses

The relative amount of electrical energy and thermal energy for boiler fuel can be varied to a limited degree. The fuel requirements listed above are for a cell liquor caustic concentration of 140 grams per liter, which is normal for this type of cell. By operating at higher cell liquor concentrations, up to about 160 grams per liter, the steam for concentration can be reduced about 10-12%, but cell current efficiency decreases and power consumption increases. The rates used are about optimum for a graphite anode cell. These rates result in a total energy consumption of 40.58 x 10^6 Btu/ton as shown below:

	10^6 Btu/ton
Electrical Power (3274 kWh) (10,500 Btu/kWh)	34.37
Boiler Fuel	9.15
Total	43.52
Hydrogen Credit	(2.94)
Net Total	40.58

2. Current Effluent Situation

a. Water Pollution

"Water pollution regulatory constraints imposed upon the chlor-alkali industry are mainly the result of Sections 304(b) and 306 of the Federal Water Pollution Control Act, as amended. The Act provides for the Environmental Protection Agency to issue effluent limitations guidelines applicable to the point source discharge of industrial wastewater. For specific industry categories, the effluent limitations guidelines are based on technical studies commonly referred to as the EPA Development Documents. The function of the Development Document is to characterize the industry, describe the sources of water pollution, the wastewater characteristics, control technology currently in use, suggested permissible effluent levels, recommended technology for their attainment, and cost estimates for the implementation of such technology. For this study, general information on the sources of wastewater, wastewater characteristics, treatment technology, and treatment cost estimates has been extracted from the Development Document pertaining to the chlor-alkali industry.*

(1) Sources of Wastewater

The diaphragm cell process for the manufacture of chlorine and caustic soda or caustic potash usually has the following raw wastes emanating from the process:

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*Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Major Inorganic Products Segment of the Inorganic Chemicals Manufacturing Point Source Category, U.S. Environmental Protection Agency, March 1974. EPA-440/1-74-007-a

- A solution of sodium hypochlorite and sodium bicarbonate from the scrubbing of chlorine tail gases (about 7.5 lb of dissolved solids/1000 lb of chlorine produced);
- Chlorinated organics from the liquification of chlorine gas (about 0.7 lb/1000 lb of chlorine produced);
- Brine wastes from the brine purification system (about 12.2 lb of dissolved solids/1000 lb of chlorine produced);
- Spent sulfuric acid from the chlorine drying process (about 4.2 lb/1000 lb of chlorine produced);
- Weak caustic and brine solution from the caustic evaporators using barometric condensers (about 9.5 lb of dissolved solids/1000 lb of chlorine produced); and
- Weak caustic and brine solution from the caustic filter washdown (about 37.5/lb of dissolved solids/1000 lb of chlorine produced).

Lead is sometimes present in the effluent as a result of cracks around protective resin seals which encase underlying lead mountings. Currently, over 30% of the industry is using anodes (DSA) which eliminate the lead discharge. Industry representatives state that another 30% are seriously considering conversion.

The mercury cell process for the manufacture of chlorine and caustic soda or caustic potash usually has similar wastes to the diaphragm cell process - the notable exception is the additional presence of mercury in the wastewater due to losses of mercury from the process. Based on a survey of 21 facilities, the Development Document sets forth a typical raw wasteload for the mercury cell process, which is shown in Table IV-3.

(2) Effluent Limitations

Based on the findings and recommendations presented in the Development Document, the Environmental Protection Agency has published "Effluent Limitations Guidelines for the Chlor-Alkali Industry."* The Effluent Limitations Guidelines will serve as the basis for the issuance of actual specific discharge permits and will directly influence the type of technology to be implemented and its associated costs.

The Effluent Limitations Guidelines sets forth three treatment levels:

- Best Practicable Control Technology Currently Available (BPCTCA) - to be implemented by 1977;
- Best Available Technology Economically Achievable (BATEA) - to be implemented by 1983; and

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*Federal Register, March 12, 1974

TABLE IV-3

RAW WASTE LOADS FROM MERCURY CELL PROCESS BASED ON A SURVEY OF 21 FACILITIES
(lb/1000 lb chlorine)

Waste	Mean	Range
Purification Muds ($CaCO_3$ 8 Mg $(OH)_2$)	16.5	0.5 - 35
NaOH	13.5	0.5 - 32
NaCl	211	15 - 500
KCl	-	-
H_2SO_4	16	0 - 50
Chlorinated Hydrocarbons*	0.7	0 - 1.5
Na_2SO_4	15.5	0 - 63
Cl_2 (as $CaOCl_2$)	11	0 - 75
Filter Aids	0.85	0 - 5
Mercury	0.15	0.02 - 0.28
Carbon, Graphite	20.3	0.35 - 340

*Depends markedly on grade of chlorine produced.

Source: "Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Major Inorganic Products Segment of the Inorganic Chemicals Manufacturing Point Source Category", U.S. Environmental Protection Agency, EPA-440/1-74-007a, March, 1974.

- New Source Performance Standards - which apply to new plants constructed before 1983 and to major changes in existing plants.

The effluent limitations are given in terms of kg of pollutants per 1000 kg of product (equivalent to lbs per 1000 lb of product), and are specified both for maximum daily levels and maximum 30-day averages. The effluent limitations are as follows:

- Diaphragm Cells - The effluent limitations restrict the discharge of total suspended solids and lead, and place restrictions on pH.

BPCTCA Level (1977)

Effluent Characteristics	Effluent Limitations	
	Maximum for any 1 day	Average of Daily values for 30 consecutive days shall not exceed -
	Metric units (kg per 1,000 kg of product)	
Total Suspended Solids	0.64	0.32
Lead	.005	.0025
pH	Within the range 6.0 to 9.0	

BATEA Level (1983)

There shall be no discharge of process wastewater pollutants to navigable waters.

New Source Performance Standards

Effluent Characteristics	Effluent Limitations	
	Maximum for any 1 day	Average of daily values for 30 consecutive days shall not exceed -
	Metric units (kg per 1,000 kg of product)	
Total Suspended Solids	0.64	0.32
Lead	.00008	.00004
pH	Within the range 6.0 to 9.0	

- **Mercury Cell** - The effluent limitations restrict the discharge of total suspended solids, mercury, and place restrictions on pH.

BPCTCA Level (1977)

Effluent Characteristic	Effluent Limitations	
	Maximum for any 1 day	Average of Daily values for 30 consecutive days shall not exceed -
	Metric Units (kg per 1,000 kg of product)	
Total Suspended Solids	0.64	0.32
Mercury	.00028	.00014
pH	Within the range 6.0 to 9.0	

BATEA Level (1983)

1. There shall be no discharge of process wastewater pollutants into navigable water.

2. A process wastewater impoundment-which is designed, constructed and operated so as to contain the precipitation from the 25-year, 24-hour rainfall event as established by the National Climatic Center, National Oceanic and Atmospheric Administration for the area in which such impoundment is located - may discharge that volume of process wastewater which is equivalent to the volume of precipitation that falls within the impoundment in excess of that attributable to the 25-year, 24-hour rainfall event, when such event occurs.

New Source Performance Standard

Effluent Characteristic	Effluent Limitations	
	Maximum for any 1 day	Average of Daily values for 30 consecutive days shall not exceed -
	Metric units (kg per 1,000 kg of product)	
Total Suspended Solids	0.64	0.32
Mercury	.00014	.00007
pH	Within the range 6.0 to 9.0	

(3) Control Technology

For both the mercury cell and diaphragm cell categories, the BPCTCA limitations require the control of specific pollutants, lead and mercury, from the wastewater prior to discharge, while the BATEA limitations for both categories prohibit the discharge of process wastewater pollutants. In complying with these limitations, the chlor-alkali industry will have to implement both end-of-pipe treatment of wastewater and various degrees of waste recovery and internal wastewater recycle.

The Development Document recommends a number of wastewater treatment and pollution abatement measures that are believed to enable the industry to comply with the various effluent limitations. These measures are summarized below:

- Diaphragm Cells

BPCTCA Level (1977)

1. Asbestos and cell rebuilding wastes are filtered or settled in ponds then land dumped;
2. Chlorinated organic wastes are incinerated or land dumped;
3. Purification muds from brine purification are returned to salt cavity or sent to evaporation pond/settling ponds; and
4. Weak Caustic (brine solution from the caustic filters) is partially recycled.

BATEA Level (1983)

Same as BPCTCA, plus

1. Waste sulfuric acid is reused or sold;
2. The hypochlorite waste is catalytically treated and reused or recovered;
3. All weak brine solution is recycled; and
4. Conversion to stable anodes.

No specific technology has been recommended for the New Source Performance Standards, but one can reasonably conclude that the BPCTCA level in conjunction with a high level of recycle would be sufficient.

- Mercury Cells

BPCTCA Level (1977)

1. Cell rebuilding wastes are filtered or placed in settling pond, then used for landfill;

2. Chlorinated organic wastes are incinerated or placed in containers and land dumped;

3. Purification muds from brine purification are returned to brine cavity or sent to evaporation/settling ponds;

4. Brine waste streams are partially recycled; and

5. Mercury effluent is recovered and reused by curbing, insulation and collection of mercury containing streams, then treatment with sodium sulfide. The precipitated mercuric sulfide is converted back to mercury for reuse.

BATEA Level (1983)

Same as BPCTCA plus

1. Waste sulfuric acid is reused or recovered;

2. The hypochlorite waste is catalytically treated and reused or recovered;

3. All weak brine solutions are recycled.

(4) Pollution Abatement Costs

Since compliance with the BPCTCA and BATEA effluent limitations can entail many combinations of end-of-pipe wastewater treatment, wastewater recycle, and in-process changes, the actual costs incurred will vary greatly among specific plants. Furthermore, there are various stages of pollution abatement measures already in-place, thus further complicating an estimate of the cost of compliance.

To reduce these complexities, the Development Document makes use of a cost model and considers the following four treatment levels:

Level A - Base level practices followed by most of the industry and exceeded by exemplary plants;

Level B - Treatment and control practices at the average exemplary plant;

Level C - The best technically and economically feasible treatment and control technology; and

Level D - Complete waterborne waste elimination.

The cost model considers a 1000 ton/day (chlorine basis) mercury cell plant and a 1000 ton/day (chlorine basis) diaphragm cell plant for the purpose of cost estimates. The cost estimates are shown in Tables IV-4 and IV-5. In each case treatment level B corresponds to BPCTCA and level D to BATEA. Note these levels are cumulative in that D includes A through C.

TABLE IV-4

WASTEWATER TREATMENT COST ESTIMATES
Diaphragm Cell Chlor-Alkali (1000 tons/day capacity - 360 days/year)

	Treatment Level			
	A	B	C	D
Capital Investment	$32,000	$46,700	$355,000	$1,076,000
Variable Costs				
Operating & Maintenance	13,500	122,500	122,500	122,500
Energy & Power	nil	1,000	1,000	1,000
Total Variable Cost	$13,500	$123,500	$123,500	$123,500
Fixed Costs				
Depreciation @ 9.1%	2,900	4,200	32,300	97,900
Taxes & Insurance @ 1.5%	500	700	5,300	16,100
Total Fixed Cost	$3,400	$4,900	$37,600	$114,000
Total Annual Cost	$16,900	$128,400	$161,100	$237,500
Return on Investment @ 20%	$ 6,400	$ 9,300	$ 71,000	$215,200
Total	$23,300	$137,700	$232,100	$452,700
Total per Unit ($/ton chlorine)	$0.065	$0.38	$0.64	$1.26
Wastewater Treatment Energy Consumption				
Electrical (kwh/yr)	nil	83,300	83,300	83,300
Thermal (10^6 Btu/yr)	-	-	-	-
Total Energy Equivalent (10^6 Btu/yr)	nil	875	875	875
Total per Unit (10^6 Btu/ton chlorine)	nil	0.0024	0.0024	0.0024

Notes:
1. Costs derived from EPA Development Document and adjusted to fit specific cases.
2. Costs for the treatment levels are cumulative, i.e., D includes A + B + C.
3. Costs have been adjusted to the 1975 level using the Engineering News Record Construction Cost Index.
4. Level A - Settling pond.

   Level B - Chlorinated hydrocarbons to disposal pit + sulfuric acid to sales, neutralization of sodium hydroxide and brine returned to system.

   Level C - Installation of chlorine burning hydrochloric acid plant for chlorine tail gas. Hydrochloric acid value is assumed to be equal to variable costs.

   Level D - Non-contact cooling substituted for barometric condensers (rough estimate).
5. Total annual cost includes cost of on-site sludge disposal. Total sludge generation = 1,350 TPY (dry basis).

TABLE IV-5

WASTEWATER TREATMENT COST ESTIMATES
Mercury Cell Chlor-Alkali (1000 tons/day capacity - 360 days/year)

	Treatment Level			
	A	B	C	D
Capital Investment	$1,736,000	$1,736,000	$2,434,000	$2,604,000
Variable Costs				
Operating & Maintenance	354,000	354,000	388,000	411,000
Energy & Power				
Electricity @ $0.012/kwh Fuel @ $0.70/$10^6$ Btu	17,000	17,000	30,200	97,000
Total Variable Cost	$371,000	$371,000	$418,200	$508,000
Fixed Costs				
Depreciation @ 9.1%	158,000	158,000	221,000	237,000
Taxes & Insurance @ 1.5%	26,000	26,000	36,500	39,000
Total Fixed Cost	$184,000	$184,000	$257,500	$276,000
Total Annual Cost	$555,000	$555,000	$675,700	$784,000
Return on Investment @ 20%	$347,200	$347,200	$486,800	$520,800
Total	$902,200	$902,200	$1,162,500	$1,304,800
Total per Unit ($/ton chlorine)	$2.51	$2.51	$3.23	$3.62
Wastewater Treatment Energy Consumption				
Electrical (kwh/yr)	1,420,000	1,420,000	1,420,000	1,420,000
Thermal (10^6 Btu/yr)	-	-	18,800	114,200
Total Energy Equivalents (10^6 Btu/yr)	14,910	14,910	33,710	129,110
Total Per Unit (10^6 Btu/ton chlorine)	0.041	0.041	0.094	0.359

Notes:
1. Costs derived from EPA Development Document and adjusted to fit specific cases.
2. Costs for the treatment levels are cumulative, i.e., D includes A + B + C.
3. Costs have been adjusted to the 1975 level using the Engineering News Record Construction Cost Index.
4. Level A - Reduction of mercury to less than 1×10^{-3} kg/kkg

   Level B - Reduction of mercury to less than 7×10^{-5} kg/kkg

   Level C - Level B + catalytic conversion of sodium hypochlorite to sodium chloride

   Level D - Level C + evaporation and reuse of sodium chloride. No effluent except cooling water. Drying sulfuric acid to other use on concentration.
5. Total annual cost includes cost of on-site sludge disposal. Total sludge generation = 8,360 TPY (dry basis).

b. Solid Waste

Solid wastes emanating from the chlor-alkali industry are the result of both the purification of raw materials and the actual production processes themselves.

Common to both the mercury-cell process and the diaphragm-cell process are solid wastes resulting from the purification of brine. Process constraints require that calcium, magnesium and sulfates be largely removed prior to electrolysis. Such removal is generally accomplished by precipitating the calcium and magnesium out of solution with caustic and soda ash. Sulfates are sometimes removed by adding barium chloride to form insoluble barium sulfate. The precipitated compounds are removed from the brine after they settle as a sludge. The brine is usually further purified by filtration, and often there are various filtration wastes such as spent filter precoat materials and filter aids. As long as satisfactory process operation makes it necessary to remove calcium and magnesium from the brine by precipitation, such wastes will be generated.

Principal sources of solid waste from the mercury cell process are:

- brine purification sludges and filtration wastes,
- used graphite cell anodes and mercury-contaminated graphite from the decomposers, and
- cell lining material and general industrial trash.

The disposal of solid waste from chlor-alkali plants using mercury cells presents certain problems because of the necessity for preventing mercury contamination. Mercury is adsorbed into the brine purification sludges and into the graphite used in the decomposers. The mercury is normally removed from the sludges by careful washing and is then precipitated as the sulfide from the wash water. The sulfide is subsequently reduced to metallic mercury for reuse. Mercury can be recovered from graphite by either roasting (retorting) or chemical leaching.

Principal sources of solid waste from the diaphragm cell process are:

- brine purification sludges and filtration wastes,
- deteriorated concrete cell hoods,
- asbestos from the cell diaphragms,
- used graphite cell anodes,
- mastic used in the bonding of carbon anodes,
- lead from cell bottoms, and
- general industrial trash.

The contact of chlorine with the hydrocarbon-based mastic can produce small quantities of chlorinated hydrocarbons.

A number of plants in the industry are taking steps to use anodes that eliminate the discharge of lead. Lead, asbestos, and chlorinated hydrocarbons are generally considered hazardous, and careful control measures are necessary for environmentally acceptable land disposal.

An estimation of the quantity of land-destined hazardous waste from the chlor-alkali industry is as follows:*

	Tons Per Year to Land Disposal	
Hazardous Constituents	Hazardous Constituents in Total Stream (dry basis)	Total Waste Stream (dry/wet basis)
Asbestos, chlorinated hydrocarbons, lead, mercury	7,700	63,000/120,000

Industry production in 1974 was 10.62 million tons of chlorine, so total dry solid waste is only 0.006 ton/ton of chlorine. The disposal cost of this material is very small, averaging about $10/ton of dry waste, or 6¢/ton of chlorine.

c. Atmospheric Emissions

Atmospheric emissions of chlorine, carbon dioxide, carbon monoxide, residual gas, or hydrogen occur from diaphragm- and mercury-cell plants in amounts that depend largely upon plant design and operation. If liquid chlorine is not produced (as in a paper mill plant), the plant will have no "blow gas," resulting from liquefaction and will have, therefore, no chlorine emissions from this source. Where liquid chlorine is produced, emissions vary according to the waste treatment system employed and the chlorine content of the blow gas.

For safety and health reasons, operating procedures are established to minimize the potential for "fugitive emissions." Consequently, the atmospheric emission points, except for accidental occurrences, are usually known and efforts are made to control the emissions as discussed in the following sections.

(1) Chlorine Emissions

- Blow Gas - When a chlorine-cell gas is compressed and cooled to produce liquid chlorine, noncondensable gases saturated with chlorine vapor are produced at the discharge of the condenser.

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*Assessment of Industrial Hazardous Waste Practices, Inorganic Chemicals Industry, U.S. Environmental Protection Agency, Contract 68-01-2246, 1975.

These gases are commonly called blow gas, sniff gas, or tail gas. The amount of chlorine emitted to the atmosphere from blow gas varies with operating conditions and the type of recovery equipment through which the stream is processed. Emissions vary with plant capacity, concentration of chlorine in the blow gas, percentage of inerts in the cell gas, and according to whether air is injected before the chlorine condenser to prevent an explosive mixture in the vent gas.

Table IV-6 shows ranges of concentrations and the amounts of chlorine that may be emitted if the emissions are uncontrolled and when various types of scrubbers are used to remove chlorine.

A typical range for the diaphragm cells is 2,000 to 10,000 lb of chlorine in the blow gas per 100 tons liquefied, or 1 to 5% of the product. Mercury-cell installations usually require more air dilution because more hydrogen is contained in the cell gas. The usual range of chlorine in the blow gas is 4,000 to 16,000 lb of chlorine per 100 tons of chlorine liquefied, or 2 to 8% of the product.

The value of this chlorine is significant and, for this reason, all but the smallest plants have for many years recovered such chlorine by either burning with hydrogen to make hydrochloric acid or by caustic scrubbing to produce bleach. Proprietary processes are also available for solvent absorption of the chlorine (one using carbon tetrachloride) and subsequent recovery of the material as elemental chlorine.

It is common practice to operate at condensing pressures and temperatures that represent an economic optimum. When there is no use for chlorine in the blow gas, and chlorine must be neutralized, it becomes economical to condense at higher pressures or lower temperatures, or both, to reduce the chlorine in the blow gas. If useful byproducts can be made, or if the chlorine in the blow gas is recycled or recovered in some other manner, it will usually be more economical to allow the percentage chlorine in the blow gas to increase in lieu of operating at relatively high pressures or low temperatures, or both.

The high operating costs encountered when chlorine in the blow gas must be neutralized and discarded have caused considerable attention to be directed to methods of recycle or recovery. This is particularly true for gas streams with large concentrations of carbon dioxide, since this compound also reacts with and consumes alkali.

Abnormal operating conditions that increase the quantities of chlorine in the blow gas are given below.

TABLE IV-6

CHLORINE EMISSIONS FORM LIQUEFACTION BLOW GASES IN DIAPHRAGM- AND MERCURY-CELL PLANTS

Type of Control	Chlorine Concentrations in Exhaust, Vol %	Emissions Factor, Lb Chlorine/100 Tons Chlorine Liquefied
None	20 to 50	2,000 to 16,000
Water Absorber	0.1 to 4.5	25 to 1,090
Caustic or Lime Scrubber	0.0001	1

Source: Environmental Protection Agency, Atmospheric Emissions from Chlor-Alkali Manufacture, January 1970 (Air Pollution Control Office Publication No. AP-30)

Operating above rated capacity - Cell manufacturers specify for a particular cell an upper current limit or cell load that determines the rate of chlorine, caustic, and hydrogen production. As technical and operating improvements have been made, cell ratings for both new and existing cells have increased. If existing chlorine condensing facilities are inadequate for the expanded plant production resulting from such improvements, the percentage of chlorine in the blow gas will increase and positive pressure may occur in the cell headers, resulting in chlorine emissions in the cell room.

Startup and shutdown - During chlorine plant startup, air is present in chlorine lines and equipment and liquefaction efficiencies are low, so that large amounts of blow gas are generated. A new cell circuit may require 8 to 24 hours to attain steady operating conditions at full load. Normally, when a cell circuit is started up, every effort is made to maintain continuous operation; at times, however, entire circuits may be shut down for major repairs or for economic reasons. To minimize the excess air in the chlorine system at startup, liquid chlorine is frequently evaporated into the chlorine headers.

- Vents from Returned Tank Cars, Ton Containers, and Cylinders - Occasionally, water and other liquids are present in returned tank cars. To ensure a clean empty car before reloading, it is common practice to apply suction to returned tank cars, as well as to cylinders and ton containers, to remove any liquid chlorine remaining in the vessel before inspection and cleaning. The amount of chlorine thus removed varies considerably, but averages about 450 pounds for a 55-ton tank car. The recovered chlorine is usually sent to the chlorine handling system, although some plants send the chlorine to a caustic scrubber to avoid upsetting their cell operation.

- Vents from Storage Tanks, Process Transfer Tanks, and Tank Cars During Handling and Loading of Liquid Chlorine - A common method of transferring chlorine involves the use of air padding. After the transfer it is necessary to vent the air, which now contains a relatively small concentration of chlorine, because the transfer is normally completed before equilibrium conditions can be reached. The amount of chlorine in the vented air varies considerably and is greater at higher temperatures. It depends also upon the shape of the vessel, the time required for transfer, and the number of transfers made.

Quantities of chlorine are flushed out with the padding air during the loading of shipping containers with liquid chlorine. Data show that the chlorine flushed out varied from 110 to 6,000 pounds per 100 tons of chlorine liquefied, with an average of 1,700 pounds. Chlorine removed during tank car loading operations is transferred to other plant uses, returned to the process, or treated in a scrubber.

In many newer plants, submerged pumps are used for the transfer of liquid chlorine. Although pumps eliminate the loss of chlorine attendant with air padding, emergency venting is necessary for pump repair and general maintenance. These emergency vents are usually connected to a caustic scrubber. It is good practice to use small pump tanks that can be isolated from large storage tanks for servicing. This practice greatly reduces emissions during pump repair.

Another method of transfer is to apply suction on the receiver or vessel to which a transfer is to be made and connect the discharge from the compressor to the vessel containing the chlorine that is to be transferred. This is somewhat similar to transfer by means of air, except that neither tank requires any venting.

- Emergency Vents - Chlorine seals and other sources of infrequent emissions are usually connected to an emergency scrubber, although in other cases these emissions are vented to the atmosphere. In either case, alarms and electrical tie-in connections are usually provided to permit prompt shutdown or changes in operating procedures to limit the duration of the emission.

  Cell room chlorine header seals - Seals on chlorine headers, provided to prevent back pressure at the cells, are usually vented to the cell house or to the outside atmosphere. Although in an emergency they must handle the full capacity of the cells connected to the header, the seals blow infrequently and for short periods. In certain locations seals are piped to a lime or caustic scrubber designed to absorb all the cell chlorine produced.

  Compressor seals - The shaft seals on liquid-seal chlorine compressors are usually piped so that a stream of sulfuric acid is fed into the compressor. Carbon-ring reciprocal compressors usually have a double stuffing box vented to a caustic scrubber or to the suction of the compressor. This effectively prevents emissions to the atmosphere.

  Storage tanks - The tank vent line is usually connected to a disposal scrubber. The relief connection from the safety valves may be vented to the atmosphere or to an emergency scrubber.

- Air Blowing of Depleted Brine in Mercury-Cell Plants - Recycled brine in mercury-cell plants is saturated with chlorine. This brine is usually vacuum treated, air blown, or both, to remove residual chlorine before resaturation. Concentrations of chlorine encountered in the vent gas are usually low and economic recovery in a water or carbon tetrachloride absorber cannot be obtained. Consequently, such gases are normally used for in-plant purposes such as water chlorination, or they are sent to lime or caustic scrubbers for disposal or vented to the atmosphere. Although air blowing of depleted brine is common, it is by no means universal. For example, certain plants air blow and retreat only a 5-10% sidestream, and several plants dispense with this procedure entirely.

- Mercury-Cell End Boxes - On certain mercury cells the discharge end box is constructed with a removable cover for servicing. End boxes are connected to a common suction header to prevent chlorine gas from entering the cell room when the covers of the end boxes are opened. Chlorine in the exhaust header is usually neutralized with lime or caustic.

(2) Other Emissions

Carbon monoxide forms a small part of the inerts in cell gas, amounting to 0.02% by volume and appearing in the same relative amounts in the blow gas. Assuming a 20-fold increase in carbon monoxide concentrations because of liquefaction of the chlorine, the carbon monoxide concentration in the blow gas would be 0.40% by volume.

The use of mercury in mercury-cathode cells produces some mercury vapor, which is emitted during cell operations. The trend toward the use of higher-strength amalgams and, therefore, lower mercury requirements has minimized mercury vapor emissions. Modern cells with steeper bottom slope, vertical decomposers, higher-strength amalgam, and increased current densites have reduced mercury inventory to slightly less than 90,000 pounds for a 100-tpd chlorine plant, about half that required by older plants. With the newer cells, daily mercury losses have decreased from 0.6 pound to less than 0.3 pound per ton of installed daily chlorine capacity. The usual range of mercury losses for typical plants in the United States has been given as 30-40 pounds per 100 tons of chlorine produced. European sources indicate that some 3% of the mercury lost is emitted to the surrounding atmosphere.

The weak (about 10-15%) sodium hydroxide solution is evaporated in a double or triple effect evaporators followed by a washing filter. The concentrated 50% solution is sold as such or further concentrated. The vapors from evaporators represent an emission source. These, however, are condensed in barometric condensers, so that the only atmospheric emissions are inert gas (air) and some steam from jet eductors.

3. Modified Anodes

a. Dimensionally Stable Anodes (DSA)

To eliminate the problems associated with the graphite anode, the industry has long worked on developing a non-consumable anode. These efforts led to the successful 1968 introduction, by De Nora in Italy, of the first commercial DSA. The anode consists of an expanded titanium metal substrate coated with precious metal/rare earth oxides. These were initially developed for mercury cells but were quickly introduced to the diaphragm cell process. In the United States they are produced and licensed by the Electrode Corporation, a joint venture of De Nora and Diamond Shamrock.

The DSA has numerous advantages which result in power savings (direct current at the cell) of up to 20% and labor savings from reduced maintenance on the cells. Chlorine quality is also improved since reactions with the graphite and organic binders is eliminated. This leads to a reduction in tail gas and in the chlorinated organics removed in the chlorine purification system. These materials, a mixture of rather indefinite composition, are now drummed for acceptable land fill disposal or incinerated. Elimination of these materials, plus elimination of the need to handle waste graphite anodes, reduces pollution problems.

Power savings result from a number of effects, the major one being the fact that anode-cathode spacing remains constant throughout use as does anode area. Thus, cell voltage does not increase rapidly with time. There is a small increase as the anode coating deactivates, which indicates a need for recoating, but the change is small compared to that experienced with graphite. A reduction in cell voltage also results from the fact that the chlorine bubbles formed on the anode are smaller and release more readily, so that less of the anode is covered with gas, which increases effective area and reduces resistance. The electrode overvoltage effects are also reduced with the coating used.

The user of the electrode has the operating option of running his plant, after installation of DSA, at the same current loading to produce the same amount of chlorine with less power per ton, or to increase current loading to produce more chlorine but at an increased consumption of power per ton of chlorine. Because capital costs and energy costs are both of major significance, the optimum lies between the two extremes.

Table IV-7 shows the estimated cost of producing chlorine in a 1000-tpd plant on the Gulf Coast. The cost plus a 20% pretax return and pollution control cost, per ton of chlorine or ECU, is \$8.35/ton, less than that shown in Table IV-2 for the graphite anode plant under the typical balance of operating conditions used here. Power consumption has been reduced by 123 kWh/ton (3.7%) and steam consumption, expressed as fuel, by 1.2×10^6 Btu/ton (13%). The latter reduction is brought about by operating the cells at a cell liquor concentration of 160 g/l* of caustic, instead of 140 g/l for graphite. Operation of the DSA at 140 g/l would decrease power use, but would eliminate the fuel savings.

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*Customary unit used in industry, therefore not expressed in English units.

TABLE IV-7

ESTIMATED PRODUCTION COST OF CHLORINE AND CAUSTIC SODA

Process: Electrolysis of Brine, DSA Diaphragm Cell
Annual Production: 360,000 tons of Chlorine
380,000 tons of Caustic Soda (100% basis as 50%)
Stream Days/Year: 360
Plant Location: U.S. Gulf Coast
Depreciation Period: 11 years (IRS Guideline)
Fixed Investment: $54,200,000

	Units Used or Annual Basis	$/Unit	Units/ton of Chlorine	$/ton Cl_2
Variable Costs				
Salt (100% as brine)	tons	2.00	1.75	3.50
Misc. Chemicals	-	0.80	1.0	0.80
Diaphragm Material	-	0.05	1.0	0.05
Cell Rebuilding Supplies	-	0.03	1.0	0.03
Power	kWh	0.012	3151.0	37.81
Fuel for Steam (Gas)	10^6 Btu	0.70	7.95	5.56
H_2 Fuel Credit	10^6 Btu	0.70	2.94	(2.06)
Cooling Water Circ.	10^3 gal	0.02	40.0	0.80
Process Water	10^3 gal	0.25	1.9	0.48
Anode Royalty	-	-	-	5.20
				52.17
Semi-Variable Costs				
Operating Labor	34 men	12,000/yr		1.13
Supervision	4 men	18,000/yr		0.20
	1 superintendent	25,000/yr		0.07
Labor Overhead	35% of Labor & Supervision			0.49
Maintenance	4% of Investment	-		6.02
				7.91
Fixed Costs				
Plant Overhead	70% of Labor & Supervision			0.98
Local Taxes & Insurance	1.5% of Investment			2.26
Depreciation	9.1% of Investment			13.67
				16.91
TOTAL PRODUCTION COST				76.99
Return on Investment (pretax)	20% of Investment			30.11
Pollution Control	See Table IV-4			0.55
TOTAL				107.65

Source: Arthur D. Little, Inc. estimate

Other savings result from elimination of graphite costs, reduction in rate of diaphragm renewal (no plugging from graphite particles) and labor savings, because less cell rebuilding is needed, and in new plants fewer, larger cells are used. A modern DSA cell would be rated at 150,000 amperes compared to 80,000 for the largest graphite anode cells. The smaller number of cells also reduces the number of bus connections and bus losses tend to decrease.

The power and energy use breakdown for the typical plant of Table IV-7 is as follows:

	kWh/ton
DC to Cell	2774
Busbar Losses	30
Total DC Power	2804
AC Power at 97% Efficiency	2891
Auxiliary Process Power	250
Power for Plant Auxiliaries	10
Total AC Power	3151
Added Power for Environmental Control	0.23 (Negligible)
Steam Use	lb/ton Cl_2
Evaporators	5447
Miscellaneous Plant Uses	700
Total	6147
Fuel equivalent at 1100 Btu/lb steam and 85% boiler efficiency	7.94 x 10^6 Btu/ton
Byproduct hydrogen fuel credit	(2.94) x 10^6 Btu/ton
Net fuel requirement	5.01 x 10^6 Btu/ton

(Compare with tabulation on page 28 for graphite anode process)

Under present commercial arrangements, the DSA are leased by Electrode Corporation to the user and recoated by Electrode Corporation. The user pays an initial fee, included in the plant investment cost shown in Table IV-7, plus a running royalty calculated as shown below.

For a power cost under 10 mills per kWh the royalty in dollars per ton of chlorine is:

3.00 + 200 (power cost, $/kWh)

Above 10 mills per kWh the royalty is:

4.00 + 100 (power cost, $/kWh)

This schedule results in a royalty of $5.20/ton at the power rate of 1.2¢/kWh used here. Thus, under the operating conditions used, the royalty exceeds the power savings but the user still has a significant cost reduction. This reduction is sufficient so that it is expected that the entire industry, with the exception of a few small plants, will soon be using DSA cells. All new capacity is being based on DSA-equipped cells.

b. Expandable DSA

The distance between the anode and the asbestos-coated cathode is one factor in determining cell voltage and power consumption. The closer the spacing the less the power consumption. With normal, rigid DSA a "working" space must be allowed to assemble the cell without scraping asbestos from the cathode as it is inserted. The expandable DSA is constructed so that the outer faces can be moved outward after the cell is assembled to allow working room for assembly and then inward for reduced spacing.

The result of this change is a reduction of about 325 kWh per ton of chlorine (about 10%) compared to the "standard" DSA configuration. This change has no effect on environmental considerations over the normal DSA unit.

Royalty arrangements for the expandable anode will split the power savings with the user, presumably on a basis to provide an incentive for their use, but specific charges are not yet known.

4. Modified Diaphragms

In addition to the significant changes in anodes, some major improvements are being introduced for diaphragms which have beneficial effects for both power consumption and environmental matters. The three most significant are discussed here in order of commercial status.

a. Polymer Modified Asbestos

This concept uses a polymer-treated asbestos diaphragm which is baked into place on the cathode. Whereas the normal deposited diaphragm swells in use (increasing electrical resistance, cell voltage, and power consumption), the modified diaphragm does not. It is also possible to use a thinner diaphragm to further reduce resistance.

Use of the diaphragm has a minor environmental benefit in that the discarded material, at the time of cell rebuilding, is in stabilized pieces instead of loose asbestos fibers. Thus, disposal is easier and safer, because the fibers resist dispersion.

Another benefit of the stabilized diaphragm is that wider DSA anodes may be used since swelling does not occur. This reduction in anode-cathode spacing can accomplish significant power savings, comparable to those achieved with the expandable anode. Based on the configuration used by Hooker for the H-4 cells, the savings compared to the standard DSA are shown in Table IV-8.

A baking oven and facilities would add about $300,000 to the capital cost of a plant, but added material costs are essentially offset by longer diaphragm life.

As noted in the table, the cell liquor concentration is 150 g/l for this comparison. At higher levels, the power savings would be slightly reduced because of reduced current efficiency. The reduction in savings may approximate 30-50 kWh/ton.

b. Polymer Membranes

A number of groups are developing microporous teflon-type polymer membranes, successfully demonstrated to date on laboratory/pilot-scale cells, which would replace the asbestos diaphragm entirely. Such thin membranes would give an energy performance equivalent to the stabilized asbestos with the "extra wide" anode shown in Table IV-8. They would have the added advantage of a much longer life and would eliminate the environmental issues associated with handling and disposal of asbestos.

The restraint on commercialization of the membranes has been the development of means for large-scale manufacture with good control of both pore size and total porosity. It is expected that these problems will be solved within the next few years.

TABLE IV-8

POWER SAVINGS EFFECTED BY STABILIZED DIAPHRAGM IN H-4 DSA CELLS

Diaphragm Type	Standard	Stabilized		
Anode Width	Standard	Standard	Wide	Extra Wide
DC Power, kWh/ton chlorine(1)	2731	2613	2525	2459
Decrease from standard, kWh/ton		118	206	272
AC Power at 97% Eff., kWh/ton		122	212	280
Power Cost Savings 1.2¢/kWh, $/ton		1.46	2.54	3.36
Added Capital Costs at 24.5%(2)		0.20	0.20	0.20
Net Savings, $/ton		1.26	2.34	3.16

(1) Differs slightly from that used elsewhere since caustic concentration is 150 g/1.

(2) 20% capital recovery, 3% maintenance, 1.5% taxes and insurance.

Source: Hooker Chemical Company and Arthur D. Little, Inc.

The use of microporous membranes is expected to have little effect on plant investment. The higher first cost of the membranes would be offset by the elimination of the present facilities for depositing asbestos and its handling.

c. Ion Exchange Membranes

There is growing interest in the use of ion-exchange membranes with high electrical conductivity and high ion-transfer rates, such as du Pont's Nafion (TM), to separate the anode and cathode compartments of the cell. These membranes would only allow transfer of positive ions to the cathode, and prevent transfer of negative ions to the anode, thus allowing production of a very pure, salt-free caustic similar to that from the mercury cell.

In the operation of such cells, the partially depleted brine is recycled for resaturation and pure water is fed to the cathode, similar to the arrangement used for mercury cells. At present, the cell units are small, such as the 45-ton-per-day unit being installed in Canada, and output caustic strength is limited to about 10% NaOH. This type of unit is well suited for replacing mercury cells in applications such as pulp mills that use a dilute caustic.

Work now underway would make this type of cell of much broader interest, because it may be possible to produce a cell capable of producing 25 to 40% caustic directly from the cell. As shown in Table IV-9, the potential energy savings over the graphite anode or DSA diaphragm cell could be significant. As shown earlier, the energy consumption for effluent control, 0.23 kWh/ton of chlorine, is negligible for these processes.

From an environmental viewpoint, the cell represents an improvement over the graphite anode/asbestos cell in the same manner as would the microporous membrane. The following waste streams generated by the graphite-anode/asbestos cell would be eliminated:

	lb/1000 lb Cl_2
Asbestos fibers	0.4
Graphite anode stubs	0.8
Evaporator purge stream	
Caustic soda	20.
Salt	50.
Water	150.

In common with other cells using DSA, the 0.45 lb/1000 lb Cl_2 of chlorinated hydrocarbons would also be eliminated.

TABLE IV-9

ESTIMATED ENERGY SAVINGS WITH ADVANCED ION EXCHANGE MEMBRANE CELL

Cell Type	Standard		Ion Exchange	
Anode	Graphite	DSA	DSA	DSA
Caustic concentration from cell	10.5%	11.5%	25%	40%
Product caustic concentration	50%	50%	50%	50%
Energy use, DC power to cells only, kWh/ton Cl_2	2894	2774	2880(1)	2980(1)
AC power at 97% efficiency	2880	2860	2969	3070
Evaporator steam fuel input 10^6 Btu/ton Cl_2	8.24	7.05	4.79	0.91
As Compared to Graphite Anode				
Power savings, kWh/ton			-89	-192
Power as 10^6 Btu/ton(2)			- 0.93	- 2.01
Fuel savings, 10^6 Btu/ton			3.45	7.33
Net Savings, 10^6 Btu/ton			2.52	5.32
As Compared to DSA				
Power savings, kWh/ton			-109	-212
Power as 10^6 Btu/ton(2)			- 1.14	- 2.23
Fuel savings, 10^6 Btu/ton			2.26	6.14
Net savings, 10^6 Btu/ton			1.12	3.91

(1) ADL estimates

(2) At 10,500 Btu/kWh

Source: Industry data and Arthur D. Little, Inc.

At the present state of development (producing 10% caustic which must be concentrated), plant costs are more expensive than normal plants. The ability to produce a higher-strength caustic will probably make them competitive.

5. Comparison of Mercury and Diaphragm Cells

To assist in providing information useful in predicting the relative viability of the mercury cell process in the United States, we have examined the process carefully and carried out an analysis of its energy requirements relative to the diaphragm cell. To keep the comparison realistic and valid for new plants that could be constructed, we have based the comparison on existing improvements which would be used in the modern design of either type of plant. Thus, for the mercury-cell basis we have used one equipped with dimensionally stable anodes and compare it with the similarly equipped diaphragm cell. Future, but developed, improvements for each are also considered.

a. Process Description

The mercury cell, although many variations exist, is usually a long, very slightly sloped trough, either rubber lined or bare steel, containing the flowing brine being electrolyzed. The cathode is a thin layer of metallic mercury completely covering and flowing down the bottom of the trough under the brine. The trough is covered, and projecting down through the top cover are many anodes, originally graphite but now DSA's. Chlorine is produced at the anodes, mixed with some hydrogen from the cathode, particularly if heavy metals are in the brine, and leaves the cell through the chlorine ducts to the drying and liquefaction system, which are exactly the same as for diaphragm cells. However, caution must be used to control the hydrogen content to prevent the explosive formation of hydrogen chloride in the cells or in the chlorine system.

At the mercury cathode, the sodium ion is discharged to form a dilute sodium amalgam. As shown in Figure IV-2, this amalgam leaves the cell and flows to the decomposer, a graphite-packed tower. Here, the amalgam is contacted with demineralized water to form a 50% caustic soda solution, mercury, and hydrogen.

$$2\ \mathrm{Na{:}Hg} + 2\ H_2O \rightarrow 2\ \mathrm{NaOH} + H_2 + 2\ \mathrm{Hg}$$

The sodium-free mercury is pumped back to the front end of the cell for reuse.

Because the caustic is formed outside of the cell it is salt-free, and can be kept iron-free since it does not have to be pumped through an evaporator system. It must, however, be treated for mercury removal, and even after treatment is not regarded as suitable for food or photographic chemical uses. The various waste streams are shown in Figure IV-2 and their disposition is given in Table IV-10.

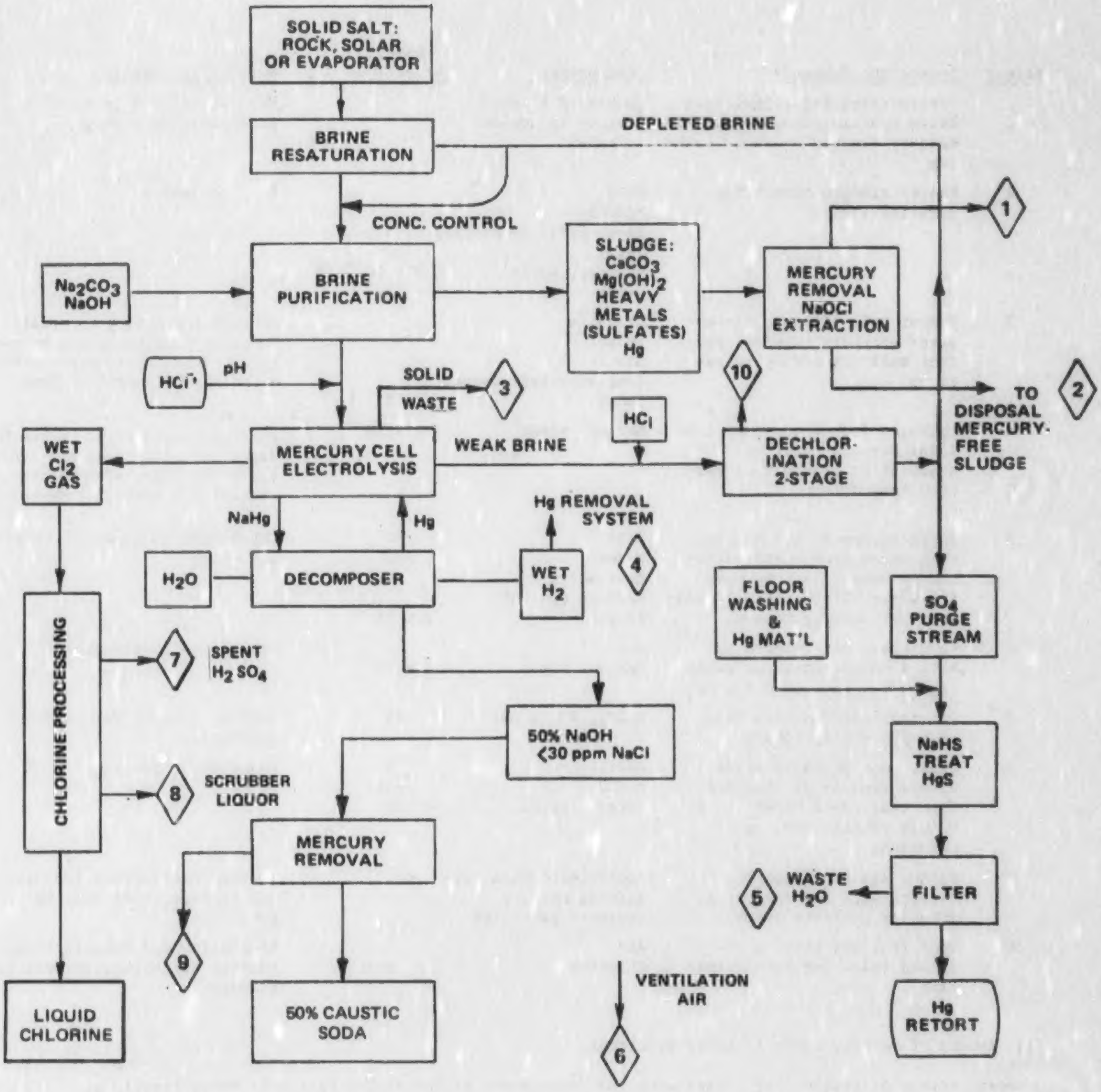
SOLID SALT: ROCK, SOLAR OR EVAPORATOR
BRINE RESATURATION
DEPLETED BRINE
CONC. CONTROL
Na_2CO_3 NaOH
BRINE PURIFICATION
SLUDGE: $CaCO_3$ $Mg(OH)_2$ HEAVY METALS (SULFATES) Hg
MERCURY REMOVAL NaOCl EXTRACTION
1
2
TO DISPOSAL MERCURY-FREE SLUDGE
HCl
pH
SOLID WASTE
3
10
HCl
WET Cl_2 GAS
MERCURY CELL ELECTROLYSIS
WEAK BRINE
DECHLORINATION 2-STAGE
NaHg
Hg
Hg REMOVAL SYSTEM
4
H_2O
DECOMPOSER
WET H_2
FLOOR WASHING & Hg MAT'L
SO_4 PURGE STREAM
CHLORINE PROCESSING
7
SPENT H_2SO_4
50% NaOH <30 ppm NaCl
NaHS TREAT HgS
8
SCRUBBER LIQUOR
MERCURY REMOVAL
WASTE H_2O
5
FILTER
9
VENTILATION AIR
LIQUID CHLORINE
50% CAUSTIC SODA
6
Hg RETORT

Figure IV-2. Mercury Cell Process

TABLE IV-10

WASTE STREAMS FROM MODERN MERCURY CELL PROCESS

Stream	Source and Comments	Components	Quantity lbs/1000 lb Cl_2	Normal Disposition
1	Precipitated impurities from brine contain adsorbed soluble mercury removed by water washing	Complexed & ionic mercury in aqueous solution		Wash water sent to sulfide precipitation system
2	Wasted sludges from brine purification	$CaCO_3$ $Mg(OH)_2$ Heavy metal hydroxides Total Mercury, Ionic(1) Water	 17 0.5×10^{-3} 55	Sent to lagoon
3	Rubber cell linings, decomposer graphite packing, etc. from cell rebuilding operations	Graphite Rubber Steel Some adsorbed mercury Total	 3	Mercury-containing materials retorted to distill out mercury for recycle; residue and other materials to land fill dump
4	Hydrogen from decomposer contains mercury vapor at equilibrium pressure of mercury temperature	Mercury vapor(1)	6.4×10^{-7}	Hydrogen refigerated to condense and recycle mercury then passed through carbon filter process for mercury recovery
5	Purge stream of brine plus wash water from purification sludge washing & housekeeping water after sulfide treatment for mercury removal	Salt Water Misc. dirt Mercury cpds.at 20 ppb(1)	80 800 0.5 2×10^{-5}	Discharged to sewer or receiving water
6	Cell house air changed to keep 50 micrograms per cubic meter max. concentration Hg	Air Mercury vapor	 2.5×10^{-3}	Discharged to atmosphere
7	Diluted sulfuric acid from chlorine drying towers	H_2SO_4, 93 to 70%	12	Sold for use or for reconcentration
8	Final vent scrubber after normal removal of chlorine from tail gas & other vents. Dilute caustic used as absorbent	NaOCl $NaHCO_3$ Water, approx.	2 nil 40	Lagooned or sewered
9	Filter aid from caustic filters used for mercury & graphite particle removal	Activated carbon containing mercury, graphite particles	< 1	Treated for mercury recovery and recycle, then sent to landfill
10	Vent from air blowing recycled brine for dechlorination	Air Chlorine	 0.45	In-plant water chlorination, caustic scrubbing, or vent to atmosphere

(1) Amount of mercury shown is after treatment.

Source: Arthur D. Little, Inc., estimates and "Assessment of Industrial Hazardous Waste Practices, Inorganic Chemicals Industry," U.S. Environmental Protection Agency, Contract 68-01-2246, 1975.

The hydrogen from the decomposer is dried, treated for mercury removal by refrigeration to condense the bulk of the mercury followed by carbon adsorption and then can be burned for fuel, sold, or vented.

In the mercury-cell process the only water losses from the brine are in the vapor leaving with the chlorine, as no evaporators are involved. Thus, the brine leaving the cell (only about 11-12% decomposed as compared to 50% in the diaphragm cell), is recirculated and must be resaturated with solid salt. Before resaturation the chlorine-saturated brine is acidified and air blown to remove chlorine and chlorates that would interfere with brine purification.

Because of the much lower percentage decomposition in the cell the brine purification system must handle about four times the volume handled in a diaphragm-cell plant. Otherwise, purification is handled in much the same way using a carbonate and caustic treatment to remove heavy metals and calcium. The sludges, precipitated under controlled conditions to minimize mercury adsorption, must be treated for mercury removal before disposal. This is done by thorough water washing on a filter with the filtrate sent to the water treatment area for sulfide treatment. Some plants use barium chloride addition to precipitate sulfate ions, others purge part of the brine to control sulfate buildup. Even though the volume of brine passing through the purification system is much larger than for the diaphragm cell, the volume of waste discharged is essentially the same. The amount of brine sludge is determined by the amount of impurities in the feed salt, not by the total volume treated.

The mercury sulfide obtained by treatment of the various waste streams is retorted, as discussed in Section IV.B.2, to recover the mercury for for reuse:

$$HgS + O_2 \rightarrow Hg + SO_2$$

This recovery operation is sometimes carried out at the chlorine plant, but the sulfide is often sent to an outside company for mercury recovery. The EPA* has sponsored work on this recovery and advanced commercial technology has been developed and used in Europe by Uhde and others.**

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*Mercury Recovery from Contaminated Waste Water and Sludges, Georgia-Pacific Corp., 1974, EPA Project No. 12040 HDU.

**European Chemical News, August 4, 1972, p. 22.

b. Cost of Production

Based upon a 1000 ton/stream day chlorine plant located on the U.S. Gulf Coast, we estimate that the fixed investment would be $58.2 million plus an added $3.6 million for mercury inventory. The latter amount is shown separately because it is regarded as non-depreciable for tax purposes but is normally amortized. About $2.6 million is required for investment in effluent treatment equipment as shown earlier in Table IV-5.

Using purchased solid salt at $12/ton delivered, and with power at 1.2¢/kWh, the production cost is estimated to be $100.13/ton, as shown in Table IV-11. The anode royalty for the DSA's is the same as for a diaphragm cell, $5.20/ton of clorine at this power cost. Again all costs are based on chlorine or the ECU. Inclusion of a minimal pretax return on investment of 20% of plant cost plus mercury cost per year, or $34.33/tons, and effluent treatment costs of $3.62/ton (Table IV-4) increases the total to $138.08/ton or ECU.

Power consumption, excluding effluent treatment, is 3712 kWh per ton of chlorine, derived as shown below:

	kWh/ton
DC power at cells	3221
Bus bar losses	65
Total DC power	3286
AC at 97% Efficiency	3387
Process use (chlorine system, Hg & brine pumps)	315
Auxiliary use	10
Total AC power	3712

Only a nominal amount of steam is used, 550 lb/ton, requiring a fuel input of 0.72×10^6 Btu at 1100 Btu/lb of steam and a boiler efficiency of 85%. The hydrogen produced, 10.7×10^3 SCF or 2.94×10^6 Btu/ton of chlorine, the same as for the diaphragm cell, cannot be fully utilized since it exceeds the heat requirements of the process. For safety reasons, only about 50% of the boiler fuel can be hydrogen, so that 0.36×10^6 Btu can be used, leaving an excess of 2.58×10^6 Btu/ton to be flared or used elsewhere. The net fuel purchases are reduced to 0.36×10^6 Btu/ton.

The ability to sell all or part of the hydrogen is a site-specific issue and depends on the local supply/demand balance for hydrogen. In most cases only modest amounts can be sold, if any. Revenue from hydrogen sales do not enter into the basic economics of a caustic chlorine plant, since such revenues are insignificant compared to those from the two major products.

TABLE IV-11

ESTIMATED PRODUCTION COST OF CHLORINE AND CAUSTIC SODA

Process:	Electrolysis of Brine, DSA Mercury Cell Process
Annual Production:	360,000 tons of Chlorine 380,000 tons of Caustic Soda (100% basis as 50%)
Stream Days/Year:	360
Plant Location:	U.S. Gulf Coast
Depreciation Period:	11 years (IRS Guideline)
Fixed Investment:	\$58,200,000
Mercury Inventory:	\$3,600,000

	Units Used or Annual Basis	\$/Unit	Units/ton of Chlorine	\$/ton Cl_2
Variable Costs				
Salt (solid)	tons	12.00	1.70	20.40
Misc. Chemicals	-	0.80	1.0	0.80
Hydrochloric Acid	pounds	0.40	30.0	1.20
Cell Rebuilding Supplies	-	0.15	1.0	0.15
Mercury	pounds	4.08	0.25	1.02
Power	kWh	3712.0	0.012	44.54
Fuel for Steam	10^6 Btu	0.70	0.72	0.50
H_2 Fuel Credit	10^6 Btu	0.70	0.36	(0.25)
Excess H_2 Fuel	10^6 Btu	-	2.58	-
Cooling Water Circ.	10^3 gal	0.02	16.4	0.33
Process Water	10^3 gal	0.25	0.4	0.10
Anode Royalty	-	-	-	5.20
				73.99
Semi-Variable Costs				
Operating Labor	29 men	12,000/yr		0.97
Supervision	4 foremen	18,000/yr		0.20
	1 superintendent	25,000/yr		0.07
Labor Overhead	35% of Labor & Supervision			0.43
Maintenance	4% of Investment			6.47
				8.14
Fixed Costs				
Plant Overhead	70% of Labor & Supervision			0.87
Local Taxes & Insurance	1.5% of Investment			2.43
Depreciation	9.1% of Investment			14.70
				18.00
TOTAL PRODUCTION COST				100.13
Return on Investment (pretax)	20% of Investment including Mercury			34.33
Pollution Control	See Table IV-4			3.62
TOTAL				138.08

Source: Arthur D. Little, Inc. estimates

As shown earlier in Table IV-5, effluent treatment adds 4 kWh per ton of chlorine to the power consumption and requires an added 0.32 x 10^6 Btu/ton of chlorine. This heat, in the form of steam, requires a fuel input of 0.41 x 10^6 Btu. As discussed before, 50% of this can be derived from hydrogen so that net added fuel to be purchased is increased by 0.2 x 10^6 Btu/ton and excess hydrogen decreased by the equivalent of 0.21 x 10^6 Btu/ton. Including these adjustments, total energy requirements are:

Total AC Power	3716 kWh/ton
Total fuel	1.13 x 10^6 Btu/ton
Hydrogen Used as Fuel	(0.57 x 10^6 Btu/ton)
Net Fuel Requirement	0.56 x 10^6 Btu/ton

c. Comparison of Energy Consumption With Diaphragm Cell

In view of the decline of the use of mercury cells for chlorine production, largely because of the understandable reluctance of the industry to risk the consequences of a plant mishap or maloperation, even though present techniques allow normal operation within all current regulations, it is desirable to analyze the energy efficiency of the process. If it offered energy advantages over the alternative cells, means could be studied to encourage its use.

In Table IV-12 the energy consumption of the mercury-cell process, both electrical and thermal, is compared with the presently used DSA/asbestos diaphragm cell and with the newer expandable anode or stabilized asbestos/wide anode diaphragm cells. A comparison is also made with the ion-exchange membrane cell, but this is to be considered approximate because of the unavailability of detailed data for this cell.

To allow properly for the total energy use, total electrical power has been converted to thermal energy by using 10,500 Btu/kWh, the U.S. average heat rate in public utility generating plants. The fuel value credit for hydrogen has been shown first, most realistically, for what can be safely used in the plant, and secondly as the total available assuming possible use in other processes.

If all hydrogen can be used, the modern mercury-cell plant uses about 2-3% less energy than the typical DSA/diaphragm plant, assuming solid salt is available for feed. However, if solid salt for plant feed must be produced from brine or solution-mined salt, salt production would require 5.6 x 10^6 Btu/ton of chlorine, making the diaphragm cell clearly advantageous. As discussed in the process description, the mercury-cell process requires a solid salt feed since only 11-12% of the salt in the brine fed to the cell is decomposed per pass and no water, except for vapor in the chlorine and purges, is removed from the system.

TABLE IV-12

ENERGY COMPARISON OF MERCURY AND DIAPHRAGM CELLS

	Mercury DSA				
	(1)	(2)	DSA Standard(3)	Wide or Expanded DSA Stabilized Diaphragm(3)	Ion Exchange (40% NaOH)(4)
Electrical Energy kWh/ton Cl_2					
DC to cells	3221	3221	2774	2459	2980
Bus & other losses	65	65	30	30	30
Total DC	3286	3286	2804	2489	3010
AC at 97% Efficiency	3387	3387	2891	2566	3103
Process AC	315	315	250	250	250
Auxiliary AC	10	14	10	10	10
Total Power	3712	3716	3151	2826	3363
Thermal Energy, 10^6 Btu/ton Cl_2					
Evaporator steam	--	--	7.05	7.05	0.91
Misc. Plant Uses	0.72	1.13	0.90	0.90	0.90
Total	0.72	1.13	7.95	7.95	1.81
Electrical as Thermal Equiv.(5)	38.98	39.02	33.09	29.67	35.31
Total Energy Use	39.70	40.15	41.04	37.62	37.12
Credit for Hydrogen Usable	(0.36)	(0.57)	(2.94)	(2.94)	(0.90)
Net Total	39.34	39.58	38.10	34.68	36.22
Hydrogen Not Usable	2.58	2.37	0	0	2.04
Total giving Allowance for all Hydrogen	36.76	37.21	38.10	34.68	34.18

(1) Plant excluding effluent control

(2) Plant including effluent control

(3) Includes effluent control

(4) Estimated from limited available data, includes effluent control

(5) 10,500 Btu/kWh

Source: Industry data and Arthur D. Little, Inc. estimates

However, the mercury cell - compared with the available technology that would be used in new plants, the expandable DSA or stabilized asbestos plus wide anode — uses 6% more energy. Comparisons based on crediting only usable hydrogen place the mercury cell at a strong disadvantage in all cases.

The advantage of the diaphragm cell from an energy viewpoint is increased if quadruple-effect evaporators, at higher capital cost, are used instead of the customary triple-effect evaporators. These would reduce energy use for evaporator stream by 20% or 1.4×10^6 Btu per ton of chlorine for the DSA diaphragm cells. Since steam use is small for the ion-exchange membrane, a quadruple-effect evaporator would not likely be considered.

From this comparison one may conclude that further development of mercury cell technology is not likely in the U.S.

V. IMPLICATIONS OF POTENTIAL INDUSTRY CHANGES

A. PROBABLE CHANGES

During the next 15-year period it is expected that the electrolytic chlorine-caustic soda industry will adopt a number of evolutionary changes that will lead to a 15% or greater reduction in energy requirements. This saving will result from a gradual conversion of major existing plants to the use of dimensionally stable anodes and stabilized or microporous polymer membranes and from the probable fact the newly constructed plants will take advantage of improved anode geometry as well as the newer types of diaphragms to achieve slightly greater energy savings.

We do not expect to see any new mercury cell plants constructed in the United States for two reasons. First, the risk of violating EPA and OSHA regulations through plant accidents, transient conditions, and the like is unacceptable to management. Second, the new developments in diaphragm-type cells provide a lower-cost, more energy-efficient process. In the near future, perhaps within five years, when the ion-exchange membrane cell has been perfected to the point where it can produce a strong caustic, we expect existing mercury-cell plants to convert, gradually, to this process. The process produces a pure, salt-free caustic, equal or superior to that from a mercury cell, particularly in that it contains no mercury, and its closed brine system fits with the existing system and system capacity in mercury-cell plants. Such conversions are now being carried out in Japan and Canada, even though production of high-strength caustic without evaporation is not now deemed commercial practice.

B. ENVIRONMENTAL IMPLICATIONS

At the present time, the industry, at least by comparison with others and excluding mercury cells, does not have severe environmental problems. Liquid effluents contain non-toxic inorganic salts and precipitates that can be lagooned and the supernatant water reused in the plant system to a major extent. However, a small amount of lead and copper salts and asbestos fibers are in these wastewater streams and are of major environmental concern from a long-range viewpoint. Probable process changes, although undertaken for energy-conservation motives, will also ease some of these environmental issues.

Table V-1 summarizes the preceding discussions of the process changes expected to take place in the diaphragm-cell process for chlorine/caustic soda manufacture and the environmental implications of these changes. The energy consumption in the form of electrical power, thermal energy and the total, expressed as equivalent thermal energy for each process, is also shown. The waste streams are numbered to key into the base process flowsheet, Figure IV-1 and Table IV-1, presented earlier.

TABLE V-1

ENVIRONMENTAL IMPLICATIONS OF CHANGES IN DIAPHRAGM CELLS

	Base Case	Process Changes			
Anode Diaphragm	Graphite Deposited Asbestos	DSA-STD Deposited Asbestos	DSA-Wide Stabilized Asbestos	DSA Microporous Membrane	DSA Ion Exchange Membrane
Waste Stream Quantities (lb/1000 lb chlorine)					
1. Brine Sludges					
Inorganic Salts(1)	18	SAME →			
Filter Aid	0.2				
Water	45				
2. Cell Rebuilding Materials					
Concrete Rubble	1	SAME →			
Graphite Rubble	2	0	0	0	0
Asbestos Fibers	0.4	0.2	0.2	0	0
3. Housekeeping, Equipment & Cleaning					
Salt	50	40	40	40	40
Caustic Soda	5	4	4	4	3
Lead	0.04	0	0	0	0
Copper	< 0.01	SAME →			
Water	600	480	480	480	480
4. Salt Purge from Evaporators					
Sodium Sulfate	10	SAME →			0
Caustic Soda	20				0
Salt	50				0
Water	150				0
5. Sulfuric Acid (Chlorine Drying)					
Dilute Sulfuric Acid	10-35	SAME →			
6. Final Vent Scrubbers					
Sodium Hypochlorite	1	0.9	SAME →		
Sodium Bicarbonate	3	2.7			
Water	40	36			
7. Chlorine Purification					
Chlorinated Organics	0.45	~ 0	~ 0	~ 0	~ 0
8. Polymer Membranes	0	0	0	< 0.05	< 0.05
Energy Use Per Ton of Chlorine or ECU					
Electrical kwh	3274	3151	2826	2826	3363
Thermal(2) 10^6 Btu	6.21	5.01	5.01	5.01	0.91
Total(3) 10^6 Btu	40.58	38.10	34.68	34.68	36.22
Fuel Value of Hydrogen not Used 10^6 Btu	0	0	0	0	0

(1) $Mg(OH)_2$, $CaCO_3$, iron and other metal hydroxides, sodium chloride.

(2) Net after maximum use of hydrogen (limited to 50% of total fuel).

(3) Electrical converted to thermal at rate of 10,500 Btu/kwh.

Source: Table IV-1 and Arthur D. Little, Inc., estimates.

Brine sludges are the impurities in the salt used as raw material which must be removed to allow proper electrolytic cell operation. These are in the form of inorganic salts, calcium carbonate and magnesium hydroxide being the principal compounds, but smaller amounts of iron and other heavy metal basic compounds are also present. The sludges are dewatered by filtering and, because of their gelatinous nature, some filter aid, such as diatomaceous earth, is used and is present in the waste cake. Salt is present because the mother liquor is a saturated brine and cake washing on the filter does not completely remove all mother liquor. The amount of sludge is directly related to the crude salt purity and for all practical purposes is not influenced by any of the process changes considered.

Cell renewal gives rise to a number of wastes which include the concrete cell bodies themselves, graphite anode stubs, and waste asbestos from spent diaphragms. It is not expected that any of the process changes will in themselves change the life expectancy of the cell body. Thus, the amount of concrete rubble sent to landfill will remain the same.

Conversion from the use of graphite anodes to DSA, in any of its variations, completely eliminates the use of graphite and this waste stream. Use of DSA reduces asbestos waste from renewal of the diaphragms since with the absence of graphite particles, they need renewal only about half as often. Conversion to either microporous polymer membranes or ion-exchange membranes completely eliminates the use of asbestos from the process. Both of these membranes are expected to have long lives, perhaps five years, and so as shown in item 7 of Table V-1, the volume of waste they will cause is estimated to be very small, less than 0.05 lb/1000 lb chlorine.

Plant housekeeping and flushing of equipment for maintenance gives rise to waterborne effluents as shown in item 3 of the table. Since the DSA-equipped cells require much less frequent renewal, there is less washing involved and it is estimated that the volume of this stream and the contained salt and caustic soda will be reduced to at least 80% of its normal amount. The ion-exchange membrane cell may produce a 40% caustic, as compared to a 10-12% from the other cells, so less evaporative equipment is needed which would lead to a further reduction in caustic in this waste stream.

As discussed, the anodes in the graphite-anode diaphragm cells are set in lead to provide electrical connections. The lead is protected from the corrosive solution in the cell by a layer of mastic, but some attack of the lead does occur. When cells are cleaned or rebuilt, small amounts of the corroded lead dissolve into the washwater and form part of the effluent. The DSA-equipped cells do not use lead for imbedding and forming electrical connections so that lead in the effluent is eliminated.

Copper compounds, less than 0.01 lb/1000 lb chlorine, get into the wastewater since the cell house atmosphere contains enough chlorine to cause some corrosion of the copper bus bars and cell connections. The process changes we envision would not alter to any appreciable degree the amount of copper contained in this waste stream.

In the part of the plant concentrating the 11-12% caustic from the cells up to 50%, a purge stream is taken to eliminate sodium sulfate from the system. This stream also contains some sodium chloride and caustic soda. Since the amount of the purge is determined by the sulfate content of the raw material salt or brine, as long as the process allows the sulfate to flow through the cell into the catholyte (dilute caustic on the cathode side of the diaphragm), there will be no change in this stream. In the ion-exchange membrane cell, however, the sulfate ions do not pass through the membrane; only the positive sodium ions are transferred to the cathode side of the membrane, which is supplied with deionized water. For this reason, the caustic solution leaving the cell is very pure, containing only insignificant amounts of materials other than sodium hydroxide and no evaporator purge is needed for the salt recycle, since there is none, or to meet product purity specifications.

The quantity of spent sulfuric acid discharged from the chlorine drying system depends on the moisture content of the chlorine gas after it is cooled, and is not influenced by any of the process changes considered here. This spent acid is normally sold for use where dilute acid can be used, or is returned to the supplier for reconcentration or fortification. Only under unusual conditions is it discharged as a waste stream.

The chlorine gas from the cells in graphite-anode-equipped cells contains carbon oxides derived to a major extent from reactions of various impurities in the brine with the graphite and air as impurities. Air enters the system through leaks, because the chlorine headers are kept under a slight negative pressure to prevent leakage of chlorine into the cell room atmosphere. The presence of these inerts results in a residual gas leaving the chlorine liquefaction equipment and following supplementary chlorine recovery processing which does contain, although primarily inerts, some chlorine. This stream is scrubbed with caustic soda to remove chlorine before the inerts are vented and the chlorine is converted to sodium hypochlorite. Carbon dioxide, also removed by the scrubbing, is converted to sodium bicarbonate. The use of DSA-equipped cells will increase the cell gas purity and decrease the volume of inerts and chlorine associated with the inerts. It is estimated that a 10% reduction, or perhaps as much as 20%, can be achieved in the final vent scrubber effluent volume.

The graphite anodes, which contain organic binders, also give rise to some chlorinated organics which leave the cell in the chlorine gas. These are removed from the chlorine after liquefaction to meet high-purity chlorine specifications. As mentioned, they are normally drummed for subsequent incineration or landfill disposal. Conversion to DSA eliminates the graphite from the process and essentially eliminates the formation of chlorinated organics in the process.

Although mercury-cell plant operators have developed processes to enable them to comply with EPA limitations on water effluents (7×10^{-5} lb/100 lb chlorine for new source standards), and discharges to the atmosphere can be held to reasonable levels, the fact that this process has no energy advantage over the newer types of diaphragm cells, and that industry is not spending funds to develop further improvements in mercury cells, is expected to limit its use to existing plants. It is probable that some plants will convert to the diaphragm-cell process, particularly when the ion-exchange membrane type is further developed, and thereby achieve a reduction in the total amount of mercury discharged to the environment by the chlorine industry.

We conclude that these expected process changes, which could cause a 15% reduction in the energy used to produce a ton of chlorine, do not result in any increased environmental problems. In fact, a reduction in the volume of waste streams and pollutants is expected.

APPENDIX A

INDUSTRY STRUCTURE

The tables and figures in this Appendix augment and complement the information presented in Chapter III, Industry Overview.

Figure A-1 shows the location of operating chlorine and alkali plants in the United States and Canada as of 1/1/75.

Tables A-1 through A-5 present details of the U.S. chlor-alkali industry by state for number of establishments, plant size, plant age, production process and production volume.

Table A-6 gives historic data on U.S. and Canadian production processes from 1946 to 1974.

Table A-7 presents a record of U.S. chlorine capacity and production from 1951 through 1974.

Finally, Tables A-8 through A-10 list U.S. producers and capacities for soda ash, caustic potash and sodium bicarbonate.

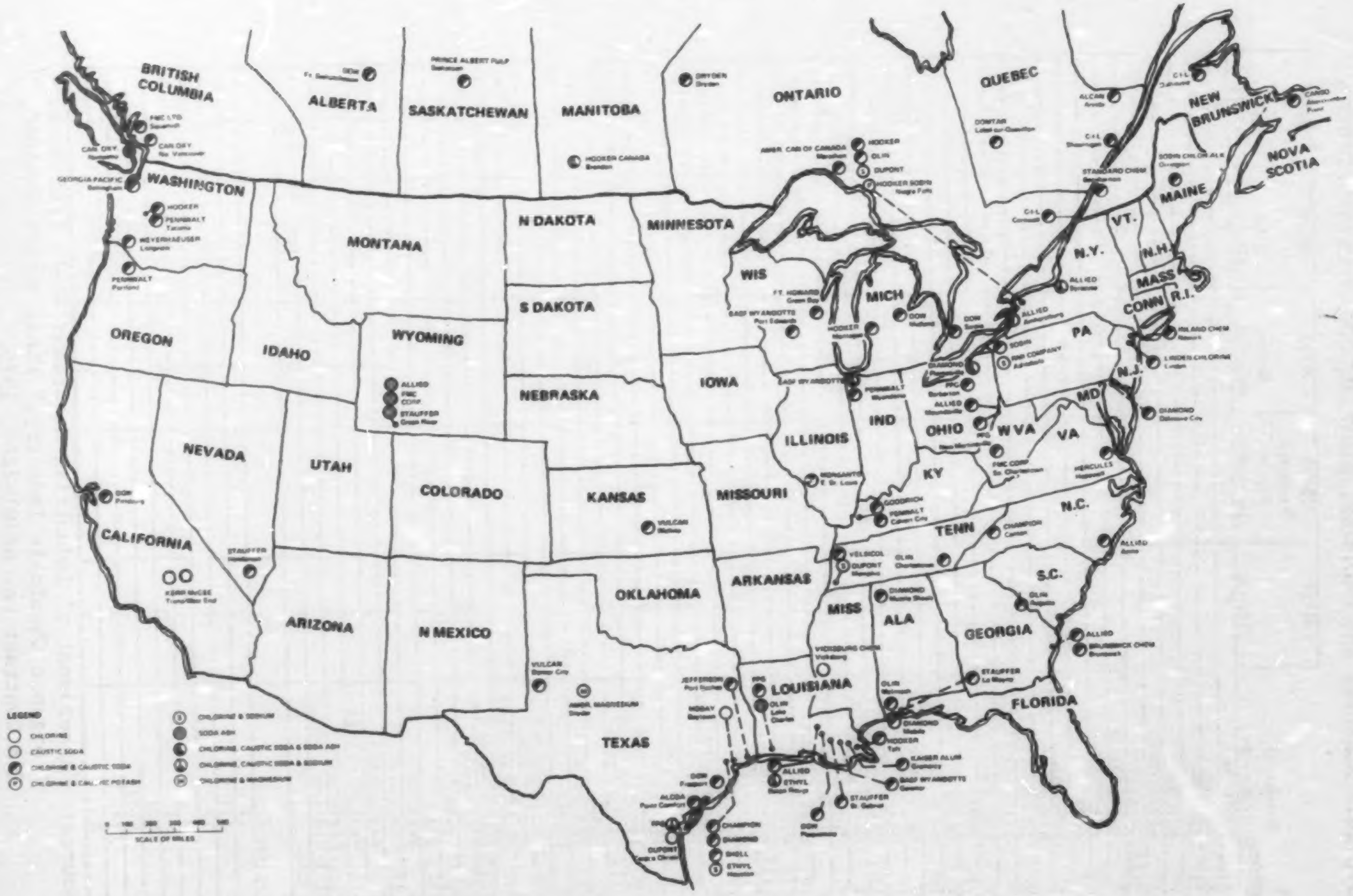
BRITISH COLUMBIA
ALBERTA
SASKATCHEWAN
MANITOBA
ONTARIO
QUEBEC
NEW BRUNSWICK
NOVA SCOTIA
WASHINGTON
OREGON
CALIFORNIA
NEVADA
IDAHO
MONTANA
WYOMING
UTAH
ARIZONA
COLORADO
N MEXICO
N DAKOTA
S DAKOTA
NEBRASKA
KANSAS
OKLAHOMA
TEXAS
MINNESOTA
IOWA
MISSOURI
ARKANSAS
LOUISIANA
WIS
ILLINOIS
MICH
IND
OHIO
KY
TENN
MISS
ALA
GEORGIA
FLORIDA
S.C.
N.C.
VA
W VA
MD
PA
N.J.
N.Y.
VT.
N.H.
MAINE
MASS
CONN
R.I.
PRINCE ALBERT PULP
HOOKER CANADA
DRYDEN
AMER. CAN OF CANADA
HOOKER
OLIN
DUPONT
HOOKER SODIUM
DOMTAR
ALCAN
C-I-L
STANDARD CHEM
SODIUM CHLORALK
FMC LTD
CAN OXY
GEORGIA PACIFIC
HOOKER
PENNWALT
WEYERHAEUSER
PENNWALT
DOW
STAUFFER
KERR McGEE
ALLIED
FMC
CORP
STAUFFER
VULCAN
AMER. MAGNESIUM
FT. HOWARD
BASF WYANDOTTE
HOOKER
DOW
PENNWALT
MONSANTO
GOODRICH
PENNWALT
VELSICOL
DUPONT
OLIN
CHAMPION
DIAMOND
PPG
ALLIED
FMC CORP
HERCULES
ALLIED
SOBIN
RMI COMPANY
ALLIED
OLIN
INLAND CHEM
LINDEN CHLORINE
DIAMOND
ALLIED
BRUNSWICK CHEM
STAUFFER
JEFFERSON
MOBAY
PPG
OLIN
Lake Charles
VICKSBURG CHEM
Vicksburg
OLIN
DIAMOND
HOOKER
KAISER ALUM
BASF WYANDOTTE
STAUFFER
DOW
ALLIED
ETHYL
Baton Rouge
DOW
ALCOA
Point Comfort
DUPONT
CHAMPION
DIAMOND
SHELL
ETHYL
LEGEND
○ CHLORINE
○ CAUSTIC SODA
CHLORINE & CAUSTIC SODA
CHLORINE & CAUSTIC POTASH
CHLORINE & SODIUM
● SODA ASH
CHLORINE, CAUSTIC SODA & SODA ASH
CHLORINE, CAUSTIC SODA & SODIUM
CHLORINE & MAGNESIUM
0 100 200 300 400 500
SCALE OF MILES

Figure A-1. Operating Chlorine and Alkali Plants in the United States and Canada - January 1, 1975

TABLE 4-1

SIC 2812 ALKALIES AND CHLORINE, DISTRIBUTION OF ESTABLISHMENTS

EPA Region	Number of Establishments	28121 Chlorine	28122 Synthetic Sodium Carbonates	28123 Sodium Hydroxide	28124 Other Alkalies	2812 as a Whole
IV	Alabama	4		4	2	4
X	Alaska					
IX	Arizona					
VI	Arkansas					
IX	California	1		1		1
VIII	Colorado					
I	Connecticut					
III	Delaware	1		1	1	1
IV	Florida					
IV	Georgia	3		3		3
IX	Hawaii					
X	Idaho					
V	Illinois	1		1	1	1
V	Indiana					
VII	Iowa					
VII	Kansas	1		1		1
IV	Kentucky	2		2	1	2
VI	Louisiana	9	2	9		10
I	Maine	1		1		1
III	Maryland					
I	Massachusetts					
V	Michigan	4	1	4	1	4
V	Minnesota					
IV	Mississippi	1				1
VII	Missouri					
VIII	Montana					
VII	Nebraska					
IX	Nevada	1		1		1
I	New Hampshire					
II	New Jersey	2		2	1	3
VI	New Mexico					
II	New York	5	1	2	3	5
IV	North Carolina	2		2	1	3
VIII	North Dakota					
V	Ohio	4	2	3	1	4
VI	Oklahoma					
X	Oregon	1		1		1
III	Pennsylvania				1	1
I	Rhode Island					
IV	South Carolina					
VIII	South Dakota					
IV	Tennessee	3		2		3
VI	Texas	11	1	9	2	12
VIII	Utah	1				1
I	Vermont					
III	Virginia	1		1		1
X	Washington	4		4		4
III	West Virginia	3		3		3
V	Wisconsin	2		2		2
VIII	Wyoming		2			2
TOTAL		67	9	59	15	74
EPA	Region I	1		1		1
	II	7	1	4	4	8
	III	5		5	2	6
	IV	15		13	4	16
	V	11	3	10	3	11
	VI	20	3	18	2	22
	VII	1		1		1
	VIII		2			2
	IX	2		2		2
	X	5		5		5

Source: "Assessment of Industrial Hazardous Waste Practices, Inorganic Chemicals Industry," Final Report SW-104C, EPA Contract No. 68-01-2246, 1975.

TABLE A-2
SIC 2812 ALKALIES AND CHLORINE. DISTRIBUTION OF PLANT SIZES

EPA Region	Plant Size, Daily Capacity (metric tons)	28121 Chlorine				28122 Synthetic Sodium Carbonates				28123 Sodium Hydroxide				28124 Other Alkalies		
		A	B	C	D	A	B	C	D	A	B	C	D	A	B	C
IV	Alabama		1	3								4				2
X	Alaska															
IX	Arizona															
VI	Arkansas															
IX	California		1								1					
VIII	Colorado															
I	Connecticut															
III	Delaware			1								1			1	
IV	Florida															
IV	Georgia		1	2							1	2				
IX	Hawaii															
X	Idaho															
V	Illinois		1									1				1
V	Indiana															
VII	Iowa															
VII	Kansas			1								1				
IV	Kentucky			2								2				1
VI	Louisiana			7	2			1	1			6	3			
I	Maine			1								1				
III	Maryland															
I	Massachusetts															
V	Michigan			4					1			4			1	
V	Minnesota															
IV	Mississippi			1												
VII	Missouri															
VIII	Montana															
VII	Nebraska															
IX	Nevada			1								1				
I	New Hampshire															
II	New Jersey			2								2			1	
VI	New Mexico															
II	New York			5					1			2			1	2
IV	North Carolina		1	1							1	1			1	
VIII	North Dakota															
V	Ohio		1	3				1	1		1	2			1	
VI	Oklahoma															
X	Oregon			1								1				
III	Pennsylvania															1
I	Rhode Island															
IV	South Carolina															
VIII	South Dakota															
IV	Tennessee			3								2				
VI	Texas		1	8	2			1			1	7	1		1	1
VIII	Utah															
I	Vermont															
III	Virginia		1								1					
X	Washington			4								4				
III	West Virginia			3								3				
V	Wisconsin			1							1	1				
VIII	Wyoming							1	1							
	TOTAL	0	8	54	4	0	0	4	5	0	7	48	4	0	7	8
EPA	Region I			1								1				
	II			7					1			4			2	2
	III		1	4							1	4			1	1
	IV		3	12							2	11			1	3
	V		2	8				1	2		2	8			2	1
	VI		1	15	4			2	1		1	13	4		1	1
	VII			1								1				
	VIII							1	1							
	IX		1	1							1	1				
	X			5								5				

KEY: A = 0-9 metric tons; B = 10-99 metric tons; C = 100-999 metric tons; D = 1000 & over

Source: "Assessment of Industrial Hazardous Waste Practices, Inorganic Chemicals Industry," Final Report SW-104C EPA Contract No. 68-01-2246, 1975.

TABLE A-3

SIC 2812 ALKALIES AND CHLORINE, DISTRIBUTION OF PLANT AGES

EPA Region	Plant Age (years)	28121 Chlorine			28122 Synthetic Sodium Carbonate			28123 Sodium Hydroxide			28124 Other Alkalies		
		A	B	C	A	B	C	A	B	C	A	B	C
IV	Alabama		4						4		1	1	
X	Alaska												
IX	Arizona												
VI	Arkansas												
IX	California			1			1						
VIII	Colorado												
I	Connecticut												
III	Delaware		1						1			1	
IV	Florida												
IV	Georgia		3						3				
IX	Hawaii												
X	Idaho												
V	Illinois		1						1				1
V	Indiana												
VII	Iowa												
VII	Kansas		1						1				
IV	Kentucky		2						2			1	
VI	Louisiana	2	5	2			2	2	5	2			
I	Maine		1						1				
III	Maryland												
I	Massachusetts												
V	Michigan		2	2			1		2	2			1
V	Minnesota												
IV	Mississippi		1										
VII	Missouri												
VIII	Montana												
VII	Nebraska												
IX	Nevada			1						1			
I	New Hampshire												
II	New Jersey		2						2			1	
VI	New Mexico												
II	New York	1	1	3			1		1	1	1	1	1
IV	North Carolina		1	1					1	1		1	
VIII	North Dakota												
V	Ohio		3	1			2		2	1			1
VI	Oklahoma												
X	Oregon		1						1				
III	Pennsylvania											1	
I	Rhode Island												
IV	South Carolina												
VIII	South Dakota												
IV	Tennessee	1	2				1	1					
VI	Texas	3	4	4			1		5	4			
VIII	Utah												2
I	Vermont												
III	Virginia			1						1			
X	Washington		2	2					2	2			
III	West Virginia	1	1	1				1	1	1			
V	Wisconsin		2						2				
VIII	Wyoming					2							
TOTAL		8	40	19	0	2	7	4	38	17	2	7	6
EPA	Region I		1						1				
	II	1	3	3			1		[illegible]	1	1	2	1
	III	1	2	2				1	2	2		2	
	IV	1	13	1				1	11	1	1	3	
	V		8	3			3		7	3			3
	VI	5	9	6			3	2	10	6			2
	VII		1						1				
	VIII					2							
	IX			2						2			
	X		3	2					3	2			

KEY: A = less than 5; B = 5 to 30; C = Over 30

Source: "Assessment of Industrial Hazardous Waste Practices, Inorganic Chemicals Industry," Final Report SW-104C EPA Contract No. 68-01-2246, 1975.

TABLE A-4
SIC 2812 ALKALIES AND CHLORINE, DISTRIBUTION OF PROCESSES

EPA Region	Process Types, No. of Facilities	28121					28122		28123			28124			
		Chlorine					Synthetic Sodium Carbonate		Sodium Hydroxide			Other Alkalies			
		A	B	C	D	E	F	G	A	B	C	A	B	H	I
IV	Alabama	4							4			2			
X	Alaska														
IX	Arizona														
VI	Arkansas														
IX	California		1							1					
VIII	Colorado														
I	Connecticut														
III	Delaware	1							1			1			
IV	Florida														
IV	Georgia	2	1						2	1					
IX	Hawaii														
X	Idaho														
V	Illinois	1							1			1			
V	Indiana														
VII	Iowa														
VII	Kansas		1							1					
IV	Kentucky	2							2			1			
VI	Louisiana	3	7	1			2		3	7	1				
I	Maine	1							1						
III	Maryland														
I	Massachusetts														
V	Michigan		4				1	1		4				1	
V	Minnesota														
IV	Mississippi					1									
VII	Missouri														
VIII	Montana														
VII	Nebraska														
IX	Nevada		1							1					
I	New Hampshire														
II	New Jersey	1	1						1	1		1			
VI	New Mexico														
II	New York	3	2	1			1	1	1	1		1	1	1	1
IV	North Carolina	1	1						1	2					1
VIII	North Dakota														
V	Ohio	1	2	1			2	1	1	2					1
VI	Oklahoma														
X	Oregon		1							1					
III	Pennsylvania											1		1	
I	Rhode Island														
IV	South Carolina														
VIII	South Dakota														
IV	Tennessee	1	1	1					1	1					
VI	Texas	2	8	1	2		1		2	8		1	1		
VIII	Utah														
I	Vermont														
III	Virginia		1							1					
X	Washington	2	2						2	2					
III	West Virginia	2	2						2	2					
V	Wisconsin								1	1					
VIII	Wyoming							2							
TOTAL		28	37	5	2	1	7	5	26	37	1	9	2	4	3
EPA	Region I	1							1						
	II	4	3	1			1	1	2	2		2	1	1	1
	III	3	3						3	3		2		1	
	IV	10	3	1		1			10	4		3		1	1
	V	3	7	1			3	2	3	7		1		1	1
	VI	5	15	2	2		3		5	15	1	1	1		
	VII		1							1					
	VIII							2							
	IX		2							2					
	X	2	3						2	3					

A = Mercury Cell; B = Diaphragm Cell; C = Down's Cell; D = HCl Process;
E = NOCl Process; F = Solvay Process; G = Bicarbonate Process;
H = Potassium Carbonate Process; I = Ammonium Carbonate Process

Source: "Assessment of Industrial Hazardous Waste Practices, Inorganic Chemicals Industry," Final Report SW 104C, EPA Contract No. 68-01-2246, 1975.

TABLE A-5

SIC 2812 ALKALIES AND CHLORINE, DISTRIBUTION OF PRODUCTION

EPA Region	Annual Production 10³ metric tons	28121 Chlorine	28122 Synthetic Sodium Carbonates	28123 Sodium Hydroxide	28124 Other Alkalies	2812 as a Whole
IV	Alabama	320		345	100	760
X	Alaska					
IX	Arizona					
VI	Arkansas					
IX	California	15		17		32
VIII	Colorado					
I	Connecticut					
III	Delaware	130		150	25	300
IV	Florida					
IV	Georgia	180		190		370
IX	Hawaii					
X	Idaho					
V	Illinois	32		59	55	150
V	Indiana					
VII	Iowa					
VII	Kansas	73		80		150
IV	Kentucky	200		220	23	440
VI	Louisiana	2,600	960	2,700		6,300
I	Maine	65		72		140
III	Maryland					
I	Massachusetts					
V	Michigan	510	750	560		1,800
V	Minnesota					
IV	Mississippi	46				46
VII	Missouri					
VIII	Montana					
VII	Nebraska					
IX	Nevada	48		53		100
I	New Hampshire					
II	New Jersey	240		260	0	500
VI	New Mexico					
II	New York	460	1,000	140.	9	1,600
IV	North Carolina	71		78	0	150
VIII	North Dakota					
V	Ohio	260	790	250	30	1,300
VI	Oklahoma					
X	Oregon	130		110		240
III	Pennsylvania				0	0
I	Rhode Island					
IV	South Carolina					
VIII	South Dakota					
IV	Tennessee	330		290		620
VI	Texas	4,000	270	2,000	6.6	6,300
VIII	Utah	73				73
I	Vermont					
III	Virginia	17		18		35
X	Washington	330		310		600
III	West Virginia	590		650		1,200
V	Wisconsin	76		80		160
VIII	Wyoming		640			640
	TOTAL	11,000	4,400	8,600	250	24,000
EPA	Region I	65		72		140
	II	700	1,000	400	9	2,100
	III	740		820	25	1,500
	IV	1,100		1,100	120	2,400
	V	880	1,500	960	85	3,400
	VI	6,600	1,200	4,700	6.6	13,000
	VII	73		80		150
	VIII	73	640			700
	IX	63		70		130
	X	460		420		840

Source: "Assessment of Industrial Hazardous Waste Practices, Inorganic Chemicals Industry," Final Report SW-104C, EPA Contract No. 68-01-2246, 1975.

TABLE A-6

CHLORINE PRODUCTION ROUTES - U.S. AND CANADA

Year	Per Cent of Total Installed Capacity					
	Canada			United States		
	Diaphragm Cells	Mercury Cells	All Other	Diaphragm Cells	Mercury Cells	All Other
1946				88.6	4.3	7.1
1956				81.6	12.4	6.0
1962	43.0	57.0	-	76.2	18.5	5.3
1963	44.3	55.6	-	74.1	20.8	5.1
1964	46.0	54.0	-	72.2	23.0	4.8
1965	45.0	55.0	-	71.2	24.2	4.6
1966	36.0	64.0	-	69.7	26.5	3.8
1967	33.2	66.8	-	69.8	26.7	3.5
1968	37.3	62.7	-	68.1	28.6	3.3
1969	43.2	56.8	-	69.2	27.9	2.9
1970	42.7	57.3	-	69.6	27.2	3.2
1971	39.9	60.1	-	69.8	27.2	3.0
1972	39.5	60.5	-	72.4	24.2	3.4
1973	53.2	46.8	-	71.8	24.6	3.6
1974	64.5	35.5	-	69.9	24.8	5.3

Source: 1946 : "Diaphragm vs Amalgam Cells for Chlorine-Caustic Production" by R.B. MacMullin, Chem. Industries, July 1947.
1956 onward : Chlorine Institute as of July 1 of year indicated.

Source: The Chlorine Institute Inc.

TABLE A-7

CHLORINE CAPACITY AND PRODUCTION IN THE UNITED STATES

Col	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
		GAS PRODUCTION						LIQUID PRODUCTION		Price
			Change from Previous Year							
Year	Capacity short Tons/Day	Short Tons	Tons	Percent	Average Tons/Day	Avg. Tons/Day Highest Month	Percent Liquefied	Short Tons	Average Tons/Day	Tank Cars Cents/Lb.
1951	5,937	2,517,913	433,752	20.81	6,898	7,409(Dec.)	46.6	1,173,753	3,211	2.70
1952	6,800	2,608,690	90,777	3.61	7,128	7,433(Jan.)	50.3	1,311,981	3,584	2.70
1953	8,200	2,797,279	188,589	7.23	7,664	7,853(Apr.)	53.0	1,483,048	4,063	2.70-2.93
1954	9,750	2,903,723	106,444	3.81	7,955	8,389(Oct.)	54.6	1,584,796	4,341	2.93
1955	10,150	3,421,107	517,384	17.85	9,373	10,270(Nov.)	54.8	1,875,552	5,138	2.93-3.05
1956	10,300	3,797,702	376,595	11.00	10,376	11,016(Dec.)	55.5	2,105,888	5,753	3.05-3.15
1957		3,947,688	149,966	3.95	10,816	11,066(Sep.)	52.9	2,090,190	5,726	3.15
1958		3,604,538	(343,130)	(8.69)	9,875	11,179(Nov.)	55.5	2,000,318	5,480	3.15
1959		4,347,118	742,580	20.60	11,910	12,555(Nov.)	51.4	2,233,329	6,119	3.15
1960	13,960	4,636,939	289,821	6.67	12,123	12,812(Mar.)	51.7	2,398,031	6,552	3.15-3.25
1961	14,405	4,600,791	(36,148)	(0.78)	12,605	13,713(Nov.)	53.9	2,478,007	6,789	3.25
1962	14,697	5,142,876	542,085	11.82	14,090	14,731(Nov.)	53.9	2,755,162	7,548	3.25
1963	15,503	5,464,080	321,204	6.24	14,967	15,733(Nov.)	53.5	2,920,127	8,000	3.25
1964	16,404	5,945,215	481,135	8.29	16,244	17,007(Dec.)	52.5	3,120,201	8,525	3.25
1965	17,245	6,517,079	571,864	9.62	17,855	19,173(Dec.)	53.5	3,484,312	9,546	3.25
1966	18,939	7,204,372	687,293	10.54	19,705	20,650(Dec.)	53.3	3,852,763	10,555	3.25
1967	21,216	7,679,868	475,496	6.60	21,041	22,491(Nov.)	51.2	3,935,754	10,783	3.35-3.45
1968	23,238	8,444,459	764,591	9.96	23,072	23,908(Dec.)	50.0	4,219,468	11,529	3.45-3.65
1969	25,124	9,375,906	931,447	11.03	25,687	27,212(Dec.)	46.7	4,381,076	12,003	3.65-3.75
1970	28,276	9,763,702	387,796	4.14	26,750	27,795(Oct.)	45.4	4,428,972	12,134	3.75
1971	29,131	9,352,437	(411,265)	(4.21)	25,623	27,178(Dec.)	47.9	4,476,242	12,264	3.75
1972	28,588	9,873,371	520,934	5.57	26,976	28,063(Nov.)	49.8	4,918,461	13,438	3.75
1973	29,643P	10,303,471P	430,100	4.36	28,229		50.8	5,238,808	14,353	
1974	30,310									

SOURCE:		
	Column 1 (Jan. 1 of year indicated)	: Chlorine Institute
	Column 2 for years 1923-1941	: "Chlorine in World War II", R.T. Baldwin, Armed Forces Chem. Jour. (Oct. 1948)
	Columns 2,6 & 8 for years 1942 onward	: Current Industrial Reports, Series M28A, U.S. Dept. of Commerce
	Column 8 for years 1914 through 1940	: Biennial Census of Manufacturers - "Made for Sale" [pulp industry not included].
	Column 10	: Oil, Paint & Drug Reporter thru 1971; Chemical Marketing Reporter 1972 onward.

Notes: Revisions are current to Dec. 74. Gas figures include amounts liquefied. Figures in parentheses are negative. Columns 3,4,5,7 and 9 are computed by the Institute from columns 2 and 8 [Basis 365 or 366 days].

Legend: P - Preliminary; R - Revised from previous report; NA - Not Available.

Source: The Chlorine Institute Inc.

TABLE A-8

U.S. SODA ASH PRODUCERS AND CAPACITIES
(short tons per year - 1973)

Producer	Location	Synthetic/Natural	Capacity
Allied	Baton Rouge, La.	S	785,000
Allied	Green River, Wyo.	N	1,100,000
Allied	Syracuse, N.Y.	S	1,000,000
BASF	Wyandotte, Mich.	S	800,000
Diamond Shamrock	Painesville, Ohio	S	800,000
FMC	Green River, Wyo.	N	1,750,000
Kerr-McGee	Trona, Calif.	N	160,000
Olin	Lake Charles, La.	S	375,000
PPG	Corpus Christi, Tex.	S	270,000
Stauffer	Green River, Wyo.	N	1,450,000
Stauffer	Westend, Calif.	N	160,000
		TOTAL	8,650,000

Source: Chemical Profiles, Schnell Publishing Co. Inc., New York.

TABLE A-9

U.S. CAUSTIC POTASH PRODUCERS AND CAPACITIES
(short tons per year - 1973)

Producer	Capacity
Allied, Syracuse, N.Y.	35,000
Diamond, Delaware City, Del.	27,000
Diamond, Muscle Shoals, Ala.	60,000
Hooker, Niagara Falls, N.Y.	53,000
Monsanto, Sauget, Ill.	60,000
Pennwalt, Calvert City, Ky.	25,000
PPG, Corpus Christi, Tex.	10,000
Sobin Chemicals, Niagara Falls, N.Y.	35,000
TOTAL	305,000

Source: Chemical Profiles, Schnell Publishing Co. Inc., New York.

TABLE A-10

U.S. SODIUM BICARBONATE PRODUCERS AND CAPACITIES
(short tons per year - 1973)

Producer	Capacity
Church & Dwight, Green River, Wyo.	100,000
Church & Dwight, Syracuse, N.Y.	100,000
Diamond Shamrock, Painesville, Ohio	28,000
BASF Wyandotte, Wyandotte, Mich.	36,000
TOTAL	264,000

Source: Chemical Profiles, Schnell Publishing Co. Inc., New York.

APPENDIX B

CHLOR-ALKALI GLOSSARY

Anode - The positive terminal of an electrical source to which electrons and negatively charged ions travel.

Brine - An aqueous salt solution.

Caustic - Characterized by the presence of hydroxyl ions in solution. Common name for sodium hydroxide.

Electrolysis - Decomposition by means of an electric current.

Ion Exchange - A reversible chemical reaction between a solid and a fluid by means of which ions may be interchanged from one substance to another.

Sniff Gas - The exhaust or tail gas effluent from the chlorine liquefaction and compression process in a chlor-alkali plant.

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